Development and validation of a Paper-based analytical device (PAD) for formaldehyde detection and its utilization in wood composites emissions

By

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Abstract

Volatile organic compounds (VOCs) are caused by different sources, including non-fully cured adhesives used to bond the pieces of wood in the fabrication of wood composites. N on-cured Phenol-Formaldehyde resins represent an important source of formaldehyde emissions. PF adhesives improve water-resistant characteristics and enhance the mechanical properties of wood composites. The impact of formaldehyde emissions has raised concern for human health and the environment and has motivated the present research work. The objective for this research is to develop a multi-pad paper-based sensor for quantifying formaldehyde in air at target concentrations. The sensor would offer a simple and cost-efficient alternative that can be used without expensive instruments and no need for experienced analysts. This analytical tool might contribute to the safety of the personnel working in the manufacturing plants of forest products such as particleboards containing formaldehyde-made resins. This multi-pad system can be developed further, to detect formaldehyde at target concentrations, Therefore, the method would be a great interest of wood panels manufacturers, inspection companies, and sectors where the below limit concentration of formaldehyde is essential. The sensor will change its color depending on the accumulated concentration, which can be readily appreciated at sight. The results of our work were assessed by image analysis, and it was possible to demonstrate that our system shows a clear reaction when exposed to formaldehyde and can be used for detection of low formaldehyde concentration values below 0.09 ppm (the limit accepted by the California Air Resources Board, CARB)

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List of Abbreviations

FA   Formaldehyde

mPAD   Multi Paper-based Analytical Device

VOCs   Volatile organic compounds

CP   Color Probe

RGB   Red, Green and Blue colors

HEX   Hexadecimal Code

Ni   Nitrazine Yellow

BX   Bromoxylenol blue

PA   Pararosaniline Chloride

CARB California Air Resources Board

Introduction

   Forest industry has been very important in Alabama due to the large number of forestall resources along its territory and keeps growing as the market for wood products is expected to increase in the mid and long term. (1) In particular, oriented strand boards (OSB) are wood composites used for higher load applications such as construction. The fabrication of OSB has grown significantly in the recent years, but there are concerns about this product releasing hazardous volatile organic gases/compounds (VOCs) during production.

The adhesives used to bond the pieces of wood in the fabrication of wood composites can cause VOCs, if the adhesives are not fully cured. For example, phenol-formaldehyde (PF) adhesives and urea-formaldehyde resins used to improve water-resistant characteristics and to enhance the mechanical properties of wood composites can emit formaldehyde, when the adhesive is not fully cured and there is residual formaldehyde. The impact of formaldehyde emissions has raised concern for human health and the environment and has motivated the present research work. The rapid and cost-efficient identification of this gas is a crucial issue that must be considered.

Volatile Organic Compounds

   VOCs are chemical carbon compounds together with oxygen and hydrogen. For example, because of their volatility, they are in the form of gases at room temperature. The industry of wood products emits VOCs, for example, in adhesives used to produce wood composites. At high concentrations or long exposure times, VOCs exposure can cause health problems, especially for people with chronic or respiratory diseases at an early age, and it can have negative impact to the

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environment also (2) It is known that house structure materials and furniture emanate gases that can affect the well-being of people.(3)

Currently, VOCs emission regulations are on the rise for manufacturers in the U.S. The wood industry is particularly affected because emissions occur mainly during drying and pressing of the wood. Treatment for air improvement requires a sizeable monetary investment when installing and operating these systems.(4,5) Currently, a typical plant can emit from 160 to 960 tons per year of VOCs in the industry. Some studies of particleboard manufacturing have shown that they are composed of tars, resins, fatty acids, acetic acid, acetone, formaldehyde, hexanal, methanol, and phenol emitted from the wood or added resins.(5)

Formaldehyde

Among other issues, rapid population growth has caused the accumulation and exposure of toxic pollutants to humans. Such is the case of carcinogens in the environment. Formaldehyde (FA) is considered a toxic element for humans stipulated by the International Agency for Research on Cancer (IARC) due to the dangers caused by being constantly exposure.(6) Being exposed to this type of pollutant has become a problem of greater magnitude in recent years. Creating detection systems in real-time FA concentration is necessary to realize it in time VOCs concentration and avoid diseases and health alterations.

Formaldehyde, also known as a methanal, formic aldehyde, metaldehyde, and oxymethylene, is a polar molecule that is very soluble in water, colorless gas with a pungent odor and a molecular size of 2.5 Å (Figure 1). The compound with a boiling point of -21 °C is a highly reactive VOC. It can be quickly photo-oxidized to carbon dioxide; it also forms formic acid when it reacts with hydroxyl radicals and bounds irreversibly to proteins.(7)
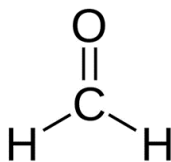
Figure 1. Chemical structure of formaldehyde

FA is ubiquitously found in air, primarily due to natural sources and anthropogenic activities, and is an essential metabolite in several metabolic routes in human cells. Among the several sources of formaldehyde emissions due to human activities(9), we can mention, for example, power plants, manufacturing facilities, and automobile exhausts (outdoor air releases), as well as building materials, consumer products, and tobacco smoke (indoor air releases). Everyday products that may cause indoor air releases are, for example, formaldehyde-containing antiseptics, disinfectants, textile, plastics, and paints.(9)

Uses of Formaldehyde

Formaldehyde is used around the world for many different industrial applications such as building and construction materials. Due to its high performance and economical application, it produces phenolic resins and melamine, working as adhesives and binders in wood production (wood composites for construction and furniture)**.** The antimicrobial properties of FA are used in antiseptics, disinfectants. FA is also used in personal care as a preservative, thus preventing the growth of bacteria and other pathogens. In health care applications, FA is used to inactivate viruses or toxins. FA finds application in transparent coat paints, tire-cord adhesives, brake pads, fuel system components, and FA-based resins for high-performance materials for exterior primers in

the automotive industry. FA is also present in the pulp and paper industry, plastics, textile fibers, paints, and food preservatives. (6,7,10)

Figure 2. General exposure to FA

Formaldehyde Health concerns

There is a vast literature signaling that prolonged exposure to formaldehyde might result in health problems such as irritation of the eyes, nose, and throat. Because of that, formaldehyde exposure and emission limits have been established by many agencies. For example, the Centers for Disease Control and Prevention (CDC) has set the typical threshold value for developing acute symptoms at 0.8 ppm after being exposed for few minutes. However, it is recognized that the health effects from exposure to formaldehyde may vary depending on individual sensitivity, and lower limits such as 0.1 ppm have been reported for chronic exposures. In 1992, the California Air Resources Board (CARB) listed formaldehyde as a toxic pollutant in California with no safe levels of exposure. Black's report finds an extensive list of regulatory agencies with corresponding exposure limits depending on the application. (11)

Commonly used products can release the FA as a hazardous air pollutant that can be dangerous for people may cause problems in the central nervous system, diseases in the respiratory and blood

system, or even cancer. (12) Being exposed to this type of pollutant has become a problem of greater magnitude during recent years. It is necessary to create detection systems in real-time FA concentration to realize it in time and avoid diseases and health alterations.

Epidemiologic studies have demonstrated an increased number of respiratory carcinoma and leukemia in humans in constant contact with formaldehyde. Now FA is considered a Known Human Carcinogen.(13)

Threshold Values for Formaldehyde Exposure

Different health regulating organizations have set threshold values for FA exposure depending on the type of exposure, ranging from values at different workplaces to homes in everyday life. Regulations for occupational inhalation exposure to FA gas have been primarily on eliminating its potential to cause sensory irritation of the eyes, nose, and throat.

Table 1. Formaldehyde emission standards for composite wood products

Regulation Agency	Threshold (ppm)	Exposure time/place
NIOSH	0.016	Indoor
WHO	0.08	Indoor
CARB	0.09	Particle board
OSHA (PEL)	0.075	8 h
OSHA (STEL)	2	15 min
AIHA ERPG-2	100	Emergency response

*NIOSH, National Institute of Occupational Safety and Health. **WHO**, World Health Organization. **CARB**, California Air Resources Board. **OSHA** Occupational Safety and Health Administration. **AIHA**, American Industrial Hygiene Association. **PEL**, Permissible Exposure Limit. **STEL**, Short Term Exposure Limit for 15 min. **REL** Recommended Exposure Limit. **ERPG**, Emergency Response Planning Guideline*

In 2016 EPA published in the Federal Register a final rule to reduce exposure to formaldehyde emissions from certain wood products produced domestically or imported into the

United States. Since 2010, formaldehyde emissions must be controlled by law because it is included in the Toxic Substances Control Act (TSCA), similar to the CARB standard limits later. Since 2019 all products related to wood composites must be labeled as CARB ATCM Phase ll or TSCA. The regulation is patterned of the California Air Resources Board (CARB) 2008 formaldehyde emissions standards. FA emission limits, required by CARB, from different products are mentioned in Table 2.

Table 2. Emission limits from wood composites required by CARB

Product	Low emission limits
Particleboard	0.09 ppm
Medium density board (MDF)	0.11 ppm
Thin MDF	0.13 ppm
Hardwood Plywood	0.05 ppm

One of the most used methods to determine the FA emissions methods is the **ASTM D6007–14**, Standard Test Method for Determining Formaldehyde Concentrations in Air from Wood Products Using a Small-Scale Chamber. The ASTM method is possible to measure very low emissions o FA. The advantage of this method is the utilization of a small chamber, saving space and time. All wood composite products can be tested with accurate results obtained by modifying the **NIOSH 3500** chromotropic acid test procedure.

Quantification methods of formaldehyde

There are several techniques for measuring the concentration of FA in air. In the case of the ASTM D6007-14, the colorimetric method is carried out inside a small chamber upon controlled conditions. Each measurement requires additional instrumentation and consumes a large number

of chemical reagents. Moreover, the standard method requires experienced technicians to get accurate results. On the other hand, the electronic sensors available in the market can quantify FA. These gadgets are user-friendly, and the measurement is rapid. However, they might not be specific, failing to measure the FA accurately.

The analytical methods for measuring airborne formaldehyde like spectrophotometric methods are most used to determine formaldehyde concentrations in indoor environments; chromotropic acid (4, 5-dihydroxy–2, 7–naphthalene sulfonic acid) and pararosaniline are the most widely used reagents. The APHA Intersociety Committee (1972) and the National Institute for Occupational Safety and Health agency have recommended a modified chromotropic acid method to estimate formaldehyde in the air. The sensitivity of this method is 0.1 µg/ml of sample solution or approximately 0.04 ppm in the sampled air. This method has some deficiencies, such as interferences from other substances, e.g., nitrogen dioxide, acrolein, and phenol, which can be encountered in indoor air. The Lawrence Berkeley Laboratory has been developing a pararosaniline technique that does not appear to be subject to interferences(14) The estimated minimal detection concentration is 0.06 ppm. Methods using other reagents are also available, but either they have not been adequately tested, or they have significant drawbacks, such as instability or interference from other chemicals,

Microwave, infrared, and laser fluorescence spectroscopy have been studied as alternatives to spectrophotometry. However, these require sophisticated maintenance and support facilities and are seldom portable. Chromatographic methods have not gained acceptance because of problems with interference and lack of sensitivity. A method for detecting formaldehyde by measuring the chemiluminescence resulting from the alkaline peroxide oxidation of formaldehyde and gallic acid

has been reported to detect concentrations as low as 0.03ppm. One drawback of this method is that it is not specific to formaldehyde

In order to make intelligent labels suitable for the monitoring of different products, such the wood composites, and safety during transport and storage and the use of low-cost, user-friendly, non-toxic, and easy-to-product materials is mandatory. Functional fibers (which is a cots efficient and ubiquitous material, characterized by high biocompatibility, biodegradability, flexibility, lightness, and chemical and biological inertness) are a suitable substrate for the assembling of platforms and devices able to respond to different physical and chemical stimuli. During this last decade, paper-based analytical devices (PADs) have attracted much attention as economic tools for in-field diagnosis, food safety, and environmental monitoring, also because they are suited for low-resource settings

Paper-based diagnostic tools (PADs)

Several sensitive electrochemical sensors, and colorimetric tests for measuring formaldehyde concentrations have been developed for measuring formaldehyde in air.(11,15,16) However, in most cases, these detection methods are expensive and require experienced analysts. Thus, simple, sensitive, and inexpensive tools for measuring gaseous formaldehyde at target concentration levels are needed. Paper-based diagnostics systems might represent a low-cost and straightforward alternative for formaldehyde detection in the air.

Humans have used paper for thousands of years. Today "paper" is the commodity material commonly used for printing and packaging, but the fibrous material used for the fabrication of paper may be used in many other applications. This fibrous and porous material (fibers) can quickly absorb liquids by capillary forces. It is flexible, foldable, creasable, biocompatible,

biodegradable, and it is easy to store and transport. Moreover, possess a large surface area that can be easily modified. After the chemical composition on the surface of the fibers is changed, the new material is referred to as Functional Fibers. *Functional fibers* bearing specially designed functionalities while preserving the excellent mechanical properties of the traditional pulp fibers produced by the pulp and paper sector (17,18) have shown the potential for the development of PADs. (17,18) One strategy to produce functional fibers is the utilization of natural polymers, which can decorate the surface of the fibers under mild conditions by the spontaneous self-assembly method. This method is simple, reproducible, and safe. In the latest forty years, different macromolecules have been tested and used in pulp and paper as dry- or wet-strength additives and as retention and fixing aids. More recently, functional fibers with the potential for advanced applications have been developed, using tailored polymers as modifying agents. These functional fibers have shown potential applications in different fields including biology, robotics, electronics, microfluidic devices, and sensors.

A multi-pad paper-based sensor would be an easy and inexpensive detection of formaldehyde in the air. The detection method should rely on the spontaneous chemical reactions between formaldehyde and the functional groups on the surface of the functional fibers and the variation of color probes that occur as a result of these chemical reactions. The multi-pad system can be developed further, to detect formaldehyde at target concentrations. The system would be of great interest to wood panels manufacturers, inspection companies, and sectors where working below the limit formaldehyde concentration is crucial.

Natural polymers

Natural polymers occur in nature and can be extracted by different methods. Examples of natural polymers are polysaccharides and proteins. Chitin is a common polysaccharide found in the exoskeleton of arthropods and cell walls of fungi. This polymer is insoluble in water, and it is constituted by a long linear chain of N-acetylglucosamine monomeric units. Chitosan is obtained from chitin, by partial *N*-deacetylation chemical reaction. The resulting molecule is the product of the conversion of more than 60% of the amide groups present in chitin, which is why the amino groups (- NH_2), whose chemical name is poly [β– (1–4) –2-amino-2-deoxy-D-glucopyranose], can contain between 6-9% nitrogen and various average molecular weights, purities and physicochemical properties such as color, solubility, viscosity, reactivity, and crystallinity. For this reason, the experimental process to deacetylate chitin is of great importance since it defines the final applications and the mechanism of action of its derivative.(20) Chitosan and chitosan derivative for the fabrication of fibers, together with color probes, can be self-assembled on cellulose blotting papers and dissolving paper with chitosan.
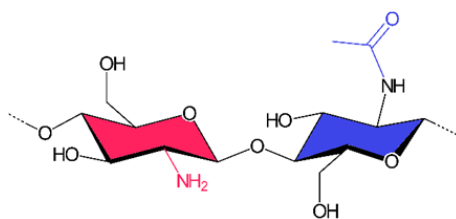

Figure 3. Chitosan structure(18)

Mannich reaction

Mannich reaction is a chemical condensation reaction that describes the spontaneous nucleophilic attack from amino functional groups to formaldehyde. The Mannich reaction is an organic reaction consisting of an amino alkylation of an acidic proton placed next to a carbonyl

functional group by formaldehyde and a primary or secondary amine or ammonia, which mechanism is illustrated in Figure 4.
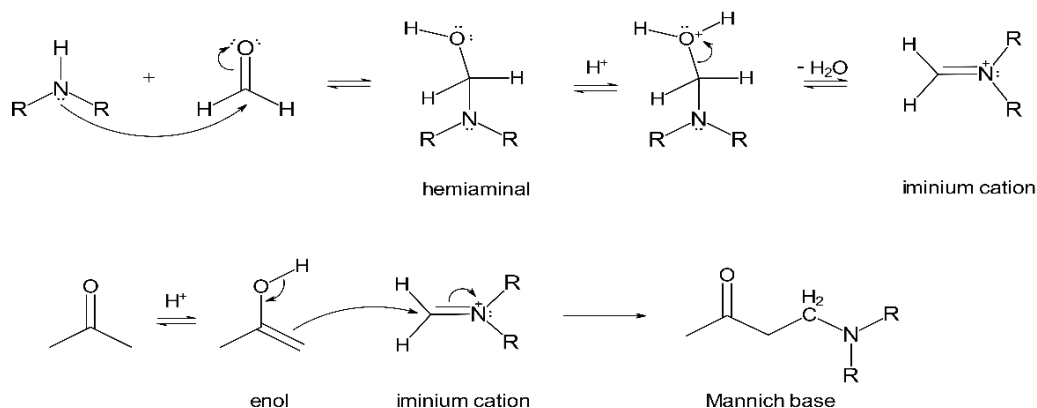
Figure 4. Mechanism of mannich reaction

The amino-functional groups found in chitosan and chitosan derivatives can react with formaldehyde through Mannich reaction. In the present work, we will describe the use of chitosan and chitosan derivatives for the fabrication of functional fibers, which can be used in the the detection of formaldehyde in air.

Rationale

With the increasing demand for wood products and with it a greater amount of pollutant gas emissions, it is necessary to have easily accessible, specific, and easy to use detection systems. The main reason for this research, results from the need to have a low cost and easy to use formaldehyde sensor, the current methods are very reagent demanding, tedious and often not specific, therefore, having a combination of PAD's and with the interaction of functionalized fiber paper and dyes, it will be possible to identify formaldehyde emissions even at low concentrations.

Hypothesis and goals

The goal for the research work described in this thesis was to develop a multi-pad paper-based sensor for quantifying formaldehyde in air at target concentrations. The colorimetric sensor would offer a simple and cost-efficient alternative that can be used without expensive instruments and no need for experienced analysts. This analytical tool might contribute to the safety of the personnel working in the manufacturing plants of forest products such as particleboards containing formaldehyde-made resins. The multi-pad indicator was fabricated using two polysaccharides combined with different dyes (color probes), which change the color at different formaldehyde concentrations. The system will specifically react to the gas emission of formaldehyde coming out of wood composites based on the Mannich reaction and color change. The sensor will change its color depending on the accumulated concentration, which can be readily appreciated at sight.

Experimental

Materials

List of chemicals: sodium hydroxide beads (ACS grade, VWR International LLC, West Chester, PA, USA), 37% formaldehyde (reagent grade, Ricca Chemical, Arlington, TX, USA), 37% hydrochloric acid (Spectrum Chemical, New Brunswick, NJ, USA), 96% v/v ethanol (Emsure®, Merck, Darmstadt, Germany), acetone (ACS grade, BDH Chemicals, Mississauga, ON, USA), disodium chromotropate dihydrate ($\geqslant$ 98.5%, TCI, Tokyo, Japan), sodium bisulfite dried (JT Baker, Radnor, PA, USA), sodium sulfite anhydrous (ACS grade, Baker & Adamson, NY, USA), 95-98% sulfuric acid (ACS grade, FCC, VWR Chemicals BDH®, Radnor, PA, USA), pararosaniline chloride (Acros Organics, Fair Lawn, NJ, USA), nitrazine yellow (Alfa Aesar, Ward

Hill, MA, USA), and bromoxylenol blue (TCI America, Portland, OR, USA), compressed air gas (ultra-zero grade, Airgas, Radnor PA, USA).

List of materials: Ahlstrom Grade 240 blotting paper, Microlon™ 200 clear polystyrene 96-well microwell plates with flat-bottom (Greiner Bio-One North America Inc., Monroe NC, USA), Unless specified, all the solids are expressed in dry-basis units.

Methods

Polymer characterization.

Amino functional groups. The functional groups that make up the surface of materials are helpful to know their properties and their interaction with other compounds. The functionalization of materials is necessary to obtain an improvement in terms of stability and compatibility with other materials. The adequate control of a surface through chemical or physical processes plays an essential role in improving the quality of the material and (its intended application). Different quantification methods can be used to obtain these results, and in this case, it was carried out carry out the AO7 method(19) which consists in mixing 50 mg of polymer with 5.0 mL of AO7 solution (0.2 mM, in water) for 5 h at room temperature, then wash the samples thoroughly with 5.0 mL of HCl solution (0.1 mM, in water) after centrifuge, followed by deionized water followed. The dye-ion complexes formed are desorbed by treating the system with 1 mL NaOH (1.0 M, in water). For the measurements, the absorbance of the supernatant was determined at 485 nm. The concentration of amino groups in the polymers (CNH2, nmol/g) was calculated according to Eq.1

$$C_{NH_2} = \left[\frac{A_{485}*V}{\varepsilon.b.m}\right].1x10^9 \quad \textbf{(Eq. 1)}$$

Where A485 is the absorbance of the pH10-supernatant at 485 nm (arbitrary units), ε is the molar absorptivity (L.mol−1.cm−1) of AO7 at 485 nm, b is the path length of the cuvette in which the

sample was contained (cm), V is the total volume of the supernatant with pH 10 (L), and m is the mass of the polymer (g). The factor $1x10^9$ was used to convert mol of amino groups per gram of dry sample into μmol/g (dry basis)

Acid-base titration. This method measured the amount of a reagent of known concentration (the titrant) consumed by the analyte (a substance to be analyzed). The volume of a known concentration (titrant) solution required to react with the analyte fully is measured in a volumetric titration. Operationally, the titration is carried out additionally and controlled from an automatic titrator that supplies the titrant, to the analyte solution until the reaction is considered complete. During titration, the point at which the amount of added titrant is stoichiometrically equivalent to the amount of analyte in the sample is defined as the equivalence point. The equivalence point of a degree is a theoretical value that cannot be determined experimentally. Its position can only be estimated by observing some physical change associated with the equivalence condition. This change is called the titration endpoint. In a titration, adding an indicator to the analyte solution is common to obtain an appreciable physical change (the endpoint) at or near the equivalence point. The most considerable changes in the relative concentration of the analyte or titrant occur precisely in the area of the equivalence point. These changes in concentration cause the shape of the indicator to change, the most typical being the appearance or disappearance of turbidity or color. The titration curves were made by adding 0.1N NaOH with an amount of 0.1 mL per minute. Using a titrator (Mettler Toledo G10S CH-8603 Schwerzenbach, Switzerland), a second derivative was plotted to see the exact pKa of the two polymers used.

Development of Functional Fibers

Different methods including dip coating, film casting and hand sheet making were tested for the decoration of bleached cellulose fibers with the polymers referred to as P1 and P2.

Dip coating. This experiment aims to achieve a uniform polymer dispersion on the paper used to achieve a constant concentration throughout the area, using the PTL-MM01 equipment from MTI Corporation, Richmond, CA, USA.
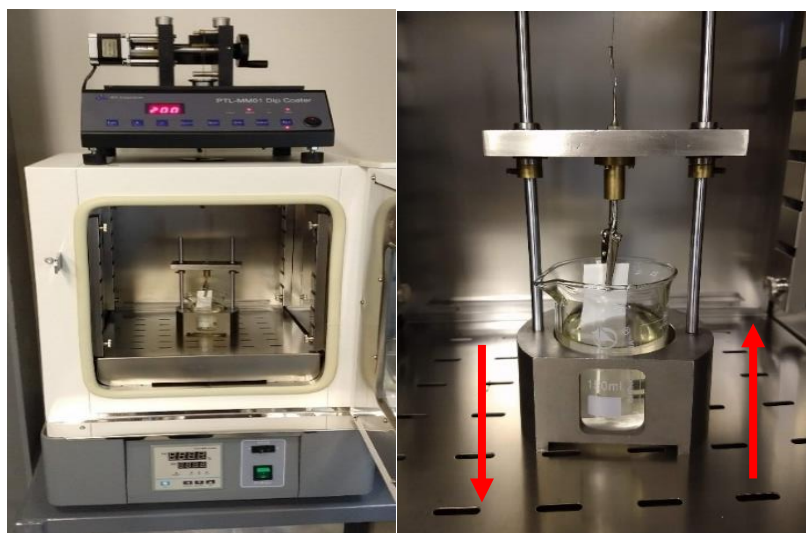

Figure 5. Dip coating performance

The dip-coating method consisted of immersing the paper at a speed of 200 mm / sec in a beaker containing the polymer and then removing it at the same speed, the excess is allowed to drain for 20 seconds, and the sample is dried in a chamber at controlled conditions of 35C and 5 hrs with 55 of RH.

Film Casting Method. In the film casting method, an MSK-AFA equipment from MTI Corporation Richmond, CA, USA (Figure 6) was used using the automatic thick film coating method, which consists of a horizontal plate on which the paper is placed, to make a film applicator

pass over it to a speed of 50 mm / sec. To later bring the paper to dry in the controlled conditions it was used a small chamber with relative humidity conditions of 60% and a constant temperature of 30 °C for 24 hours.
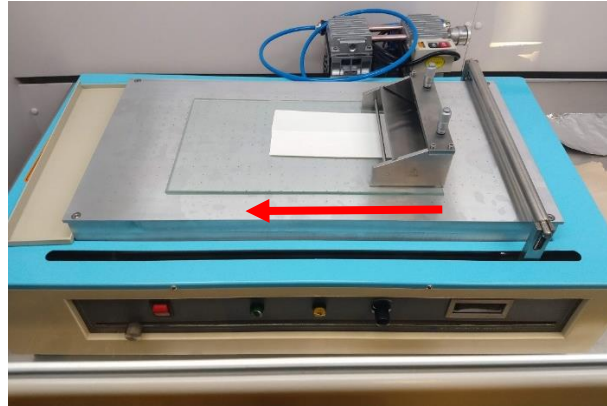
Figure 6. MSK-AFA automatic thick film coater

Figure 7. Chamber for drying samples

Paper Hand Sheet making. Paper hand sheets were fabricated following the procedure described in the Tappi standard T205 sp-02 (Forming hand sheets for physical tests of pulp) in a hand sheet forming machine (Figure 8). This procedure describes a method of forming test hand sheets at an oven-dry weight of 60 g/m^2 for determining the physical properties of pulp. Cellulose fibers modified with polymer 1 and polymer 2 were used for preparing functional hand sheets.

Figure 8. Sheet machine

Briefly, the functional fibers were suspended in distilled or deionized water to obtain 2000 ml suspension with 1.2% consistency at 20 ± 2 °C, and subsequently, the fiber bundles were dispersed in a standard disintegrator at the range of 3000 rpm for 7 min.

The amount of fresh stock suspension needed for one sheet was transferred to the hand sheet machine and water was added until the depth is about 350 mm above the surface of the forming wire. The fiber suspension was homogenized using a perforated stirrer. After the stirrer was gently removed and after a pause of 5 ± 1 s, during which time the surface of the liquid should become almost motionless, the machine's drain fully open with a rapid movement and the water was drained through the sheet under suction from the water leg.

After opening the sheet machine, two pieces of standard blotting paper centrally were placed on the drained sheet with the felt, smoother side of the lower blotter against the wet sheet. The flat couch plate was laid on the center of the blotters and the couch roll was gently placed on the middle

of the plate. The roll was rotated on top of the blotters, first backward and then forward, five times in 10 ± 2 s, with no pressure being applied except the weight of the roll. As described in the standard method, the roll should come within less than 5 mm of the edge of the plate each time. After the fifth forward rotation, the roll was rotated back to the middle lifted off.

Pressing step. a couch blotter sheet was placed on top of a press template. Then the hand sheet was placed on top, and a dry blotter was added. The process was repeated so that all sheets from a given pulp were stacked together in the press. The stack was covered with a second press template and centrally located on the press.

Place the cover of the press in position and screw the wing nuts hand tight. During a period of 30 s, slowly raise the pressure to 345 kPa (50 psi). Maintain this pressure for an additional 5 min. Release the pressure and remove the press cover. This step is repeated by changing the plotters for dry ones and then pressing for 2 min.

Hand sheets drying. Immediately after the hand sheet formation, the press blotter on top of each test sheet was discarded and each plate with its attached test sheet was placed into a drying ring with care, so that each sample is uppermost and in contact with the rubber seal of the following ring above it. A heavyweight (about 25 lbs. is suitable) was placed on top of the stack of rings. or clamp them together with a suitable clamping system.

The sheets were dried from the wet state to equilibrium in a 50% RH, 23°C conditioned room, and then stored until further use in a closed cabinet protected from light.

Modification of the surface pH of handsheets. The handsheets modified with P1 and P2 showed an acidic surface pH. For this reason, it was necessary to adjust the surface pH of the handsheets before the application of the color probes. It was decided to use the dip-coating technique to change

the surface pH of the functional fibers, using NaOH solutions at concentrations in the range from

0.011 M and 0.012M. Using the NaOH solutions, it was possible to achieve a desired surface pH

and thus impregnate the color probes to get the target color. After that, the papers were dried in an

oven at 35 °C for 5 hours. The dip-coating equipment used is the PTL-MM01 equipment from

MTI corporation

Color probes survey

One of the aims of the work described in this thesis was to utilize functional cellulose fibers

to develop an mPAD to detect low formaldehyde concentrations in the air. For that purpose, it was

necessary to identify different fiber modifying agents, including different color probes (Ci) and

polysaccharide derivatives (Px). A set of experiments was carried out in samples to make the

selection simpler. Also, it enabled the rapid identification of the best reaction conditions for the

selected compounds, including pH values and concentration range.

 Three were selected for the color probes survey: bromoxylenol blue (C1), nitrazine yellow (C2),

and pararosaniline chloride (C3). The selection was made based on its chemical structure (Figure

9) and the possible interaction with the functional groups on the functionalized fibers and the

formaldehyde.
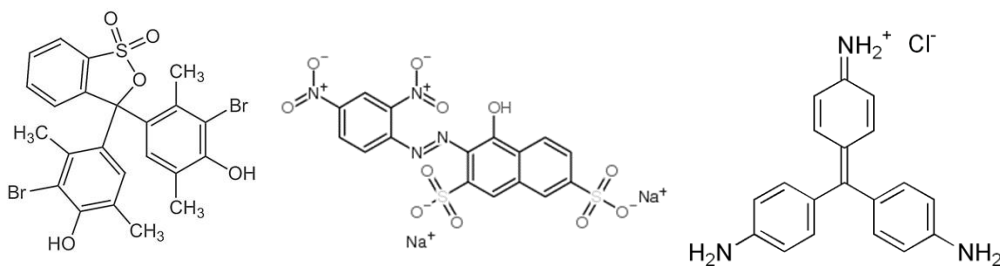
Figure 9. Chemical structure of CP1, CP2 & CP3, respectively

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Quantification color change based on pH

For the measurement of the percentage of color change (%CC) in the presence of formaldehyde, 1mg/ml solutions of the samples were prepared. For CP1 20% v/v of acetone was used. For CP2 the color probe was dissolved in water and for CP3 ethanol was used. After the samples are prepared, the pH is modified from 5 to 10 to get different range of colors, the pH is added using an automatic titrator Mettler Toledo G10S CH-8603 Schwerzenbach, Switzerland, by adding NaOH 0.1M

Color analysis. The image analysis was performed by using FIJI software to measure color intensity. The analysis performed by selecting three clear points of color to measure RGB, the size of each point was 100 pixels, then, an average of the three points was calculate and compare with the measure of the whole PAD and it provides a histogram of color intensity, using red, green and blue (RGB) as a base. having the colors quantified, an intensity difference is made and with this is possible to know the percentage of color change. To get the images the samples are scanned using an Epson Perfection® V39 scanner Model J371A (Seiko Epson Corp. Indonesia). The RGB values of each sample and the RGB values (Figure 10) of the control samples, at the same pH, were used to calculate the percentage of color change (%CC) (Eq. 2)

$$\%CC = \frac{ACV_{sample} - ACV_{control}}{ACV_{control}} \times 100 \quad \textbf{(Eq. 2)}$$
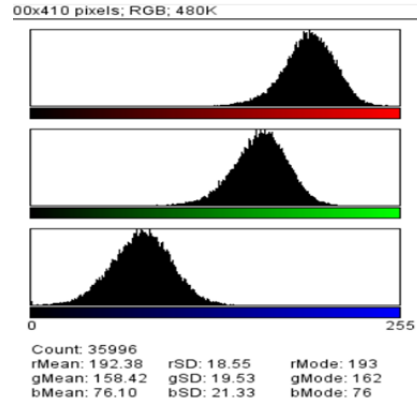
Figure 10. Example of RGB intensities in FIJI software

Conversion of RGB values to Hexadecimal code (HEX)

RGB color code values are based on the number system we are most familiar with, the decimal number system. The decimal number system is a Base-10 system, which means that there are 10 unique characters used to define the numbers. The 10 characters used are the numbers 0 - 9. Hexadecimal color code values, by comparison, are based on the hexadecimal number system. The hexadecimal number system is a Base-16 system, which means that there are 16 unique characters used to define the numbers. The 16 characters used are the numbers 0 - 9, and the letters A - F. RGB color code values are based on the number system we are most familiar with, the decimal number system. The decimal number system is a Base-10 system, which means that there are 10 unique characters used to define the numbers. The 10 characters used are the numbers 0 - 9. Counting is done the same way in both systems. The first number is 0 and is counted to the last digit. For the decimal number system, this digit is 9. For the hexadecimal number system, this digit is F. Sometimes, a 0 is written in front of these values. Once you reach the last digit, you start counting again, this time with the initial digit as the next digit in the system (which is 1 for both the decimal and hexadecimal number systems). Below is a table to help show the difference between the two number systems:

Table 3. Comparison of decimal and hexadecimal color codes

Decimal	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Hexadecimal	0	1	2	3	4	5	6	7	8	9	A	B	C	D	E	F

And following the equation below for each RGB value:

$R = \dfrac{color\ value}{16}$, If the result gives decimals, multiply by 16 **(Eq. 3)**

$G = \dfrac{color\ value}{16}$, If the result gives decimals, multiply by 16 **(Eq. 4)**

$B = \dfrac{color\ value}{16}$, If the result gives decimals, multiply by 16 **(Eq. 5)**

For example, the bright blue showed in Figure 11 below, is defined by the RGB system as (0,151,169). This means that in the Hexadecimal color system, the bright blue color will be defined as: **RR** (0/16) = 00 → calculated 0/16 = 0

GG (151/16) = 97 → calculated as 151/16 = 9.4375 → 9 + 0.4375x16 → 9 + 7

BB (169/16) = A9 → calculated as 169/16=10.5625 → 10 + 0.5625x16 → A + 9

Red	Green	Blue
R= 255	R= 0	R= 0
G= 0	G= 128	G= 0
B= 0	B= 0	B= 255
HEX= #F0000	HEX= #008000	HEX= #0000FF

Figure 11. RGB and HEX code for red, green, and blue colors

Once the RGB values of each PAD were obtained, we proceeded to make the conversion to hexadecimal code to recreate the color values using the XLSM (Excel Macro-Enabled Workbook) format code, with Visual Basic programming language (20).

Measurement of the FA concentrations in air using our paper-based sensor

The concentration of FA in air can be measured using our paper-based FA diagnostic tool. For the measuring the FA concentration in unknown concentrations and thus to know the response to different concentrations, the origin software was used to create a spline interpolation with the known data and with this, to have a smoothed curve, when obtaining the data, a grade two polynomial fitting was performed to create an equation for each RGB color with different pH and FA concentrations exposed.

For measuring the concentration of FA in air, a grade 2 polynomial fitting was created by using the data obtained from spline following the equation for each sample:

$$y = ax^2 + bx + c \quad \textbf{(Eq. 6)}$$

Quantification of %CC based on formaldehyde content

For each combination of color probe and polymer, a 1:1 CPi/Px solution was prepared by mixing. The resulting CPi/Px solutions' pH was adjusted either with NaOH (1N, in water) or HCl (1N, in water). Then, 150 µl of the CPi/Px solution was pipetted into wells in 96-well plates. Each row in the plate contained a CPi/Px solution with the same pH value, whereas the pH value of different rows differs from 4 to 10, with one unit increment between adjacent rows. Subsequently, volumes of formaldehyde solution (3.7%, in water) from 0 to 45 µl, with 5 µl increments between adjacent columns, were added to each plate. Different volumes of ultrapure water, from 45 to 0 µl, with a decrease of 5 µl between each column, were added to the same plates. The final configuration of the well plate is shown in Figure 12, showing the different volumes of 3.7% formaldehyde solutions (FA) and ultrapure water (H_2O) added to each well containing 150 µl of a CPi/Px solution at the pH indicated on the right side of the illustration. Column 2 describes

the composition of the control samples at the different initial pH values. CPi, color probe i. Px, and polymer x.

FA (µl) →	0	5	10	15	20	25	30	35	40	45		
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
A												
B		150	150	150	150	150	150	150	150	150	150	
C		150	150	150	150	150	150	150	150	150	150	
D		150	150	150	150	150	150	150	150	150	150	
E		150	150	150	150	150	150	150	150	150	150	
F		150	150	150	150	150	150	150	150	150	150	
G		150	150	150	150	150	150	150	150	150	150	
H		150	150	150	150	150	150	150	150	150	150	

pH ↓ : A(—), B 4, C 5, D 6, E 7, F 8, G 9, H 10

H_2O (µl) → : 45 40 35 30 25 20 15 10 5 0

Figure 12. Experimental design for well plates

Application of Color Probes onto Functional Fibers

Spray method. The spraying method of different CPi solutions on the paper samples was also tested. In this case, the spray of the solution on the paper was made with an airbrush (Campbell Hausfeld, China) with a 0.013 in the nozzle, free air delivered cubic feet per minute (CFM) of 0.3 at 40 psi, and a pressure range from 20 to 50 psi (Figure 13), connected to a Craftsman® 6-gallon single stage portable electric air compressor with 2.6 standard cubic feet per minute (SCFM) at 90 psi (Jackson TE, USA). In all cases, the sample was dried in a chamber with 55% RH, 35°C controlled conditions for 5 hours, after applying the color probe. The different samples were stored in glass vials in a clean chamber at room temperature and protected from sunlight until further use.

Figure 13. Airbrush kit for spraying the color probes on the paper sheet surfaces

Estimation of standard error

Each colored PAD was measured in 10 repetitions, quantifying the RGB of each one, and when the values were obtained, the standard error was calculated using the following equation

$$Standard\ error = \frac{s}{\sqrt{n}} \quad \textbf{(Eq. 7)}$$

Where: s = standard deviation of sample

√n = size of the sample

Quantification of Formaldehyde in Air

This standard test method measures the formaldehyde concentrations in air from wood products under defined test conditions of temperature and RH. The quantity of formaldehyde in an air sample from the small chamber is determined by modifying the NIOSH 3500 chromotropic acid test procedure. The measurements are developed in a designed stain steel chamber with 226cm3, using low airflow and make-up air coming from a pure air tank and passed through a carbon activated filter. The design of the chamber follows the recommendations of the standard method ASTM D6007–14 and was designed with the suggested specifications, using stainless steel material, a self-sealing door, with a volume within the allowed range. As well, pure air is used with an activated carbon filter and flow regulator. At the sampling area, a flowmeter is installed, and two impingers work as a sampler.

Procedure: The chamber was purged with clean air using an air tank to reduce the background formaldehyde concentration to below 0.02ppm. The PAD's were placed in a Petri dish separated by 10 cm each simulating the wood samples suggested by the standard. The chamber temperature was set at 25C and 50+/- relative humidity, then the air was pumped for 30 minutes in two rounds. For the air sampling, lines were purged for 1 minute. At the sampling station, air was bubbled through a single impinger containing 20 ml of a 1% sodium bisulfite (NaHSO3) solution. A filter trap was placed between the impinger and the flowmeter. The calibrated flowmeter was adjusted to maintain an average air flow rate of 1 ± 0.05 L/min for 30 min.

$$ppm = \frac{FA}{chamber\ volume} \quad \textbf{(Eq. 8)}$$

Figure 14. Components of the small chamber

Calibration curve. A 1 % sodium bisulfite (NaHSO$_3$) solution was prepared by dissolving 10 g of NaHSO$_3$ in a 1000 mL volumetric flask and diluting it to the mark with distilled water. This solution is stable at room temperature and was prepared weekly.

Eight standard solutions were prepared in 200 mL volumetric flasks by pipetting the following amounts of solution "B" followed by diluting to the mark with 1% sodium bisulfite (NaHSO$_3$).

Table 4. Preparation for calibration curve

Flask number	Solution B (mL)	Formaldehyde (µg/mL)
1	0.00	0.000
2	5.00	0.125
3	7.00	0.175
4	10.00	0.250
5	12.00	0.300
6	16.00	0.400
7	20.00	0.500
8	30.00	0.750

Concentration of each flask is calculated as follows:

flask FA concentration (µg/mL) = C_B (µg/mL) x Solution B added (mL) ÷ 200mL **(Eq. 9)**

Pipet a 4 mL aliquot from each flask specified was pipetted in A into three 25ml flasks for triplicate analyses. And then added 0.1 mL of 1 % chromotropic acid reagent to each flask. After, the addition of 6.0 mL concentrated sulfuric acid (H_2SO_4) into each flask and allowed to flow down the side of the flask. Allow the volumetric pipet to drain. The spectrophotometer was standardized using distilled water at 580 nm. The instrument was zeroed using the reagent blank, and the absorbance of the reagent blank was subtracted from the absorbance of the standard solutions. The absorbance was read at 580 nm for each standard prepared. Absorbance was plotted against micrograms of formaldehyde in a color-developed solution

Measurements of formaldehyde concentration using an electronic sensor

A Temptop M2000 electronic sensor (San Jose CA. USA) was used to monitor the concentration of formaldehyde inside the small chamber during the measurements performed using the standard method ASTM D6007-14. The measurements were gathered every minute for 1 hour.

Figure 15. Temptop M2000 electronic FA sensor

Measurement of formaldehyde in air using our multi-PADs system

The color change on each PAD exposed to a known concentration of formaldehyde was analyzed using image analysis. For that purpose, the PADs were scanned using an Epson Perfection® V39 scanner Model J371A (Seiko Epson Corp. Indonesia) to quantify the color change on each PAD after being exposed to a known formaldehyde concentration, each PAD was scanned with. The pads were scanned before being exposed to formaldehyde and after an hour exposition to a known formaldehyde concentration.

Results and discussion

Polymer characteristics

In the present work two different types of polymers referred to as P1 and P2 were utilized as fiber modified agents. The number of functional groups per gram of polymer were determined

using the AO7 method described before. According to the results showed in Table xx, the polymer P1 possess a larger number of amino ($-NH_2$) functional groups available for establishing ion pairs with the AO7 dye. The values agree with the expectations as the polymer P2 should contain lower number of $-NH_2$ groups and relatively larger number of stronger Schiff bases along the polysaccharide chain.

Table 5. Quantification of amino functional groups in P1 and P2 using AO7 method

Polymer	pH	Amino functional groups
P1	pH3	83.85 nmol/g
P2	pH3	15.72 nmol/g
P1	PH10	457.31 nmol/g
P2	pH10	177.84 nmol/g

Half-equivalence point of P1 and P2 (pK1 and pK2). Titration with NaOH have been performed to determine the pKa values of P1 and P2. The pKa values are defined as the negative logarithm base ten of the acid dissociation constant. These values provide very useful information about the week conjugated acid functional groups, which interact directly with formaldehyde and can affect the protonation of the chromophore groups in the selected dyes, in the polymers P1 and P2. According to the results shared in Figure 16, the pKa value of P1 was 8.5, whereas pKa value of P2 was 8.1. As it will be demonstrated later, the small difference in pKa value is enough to get a different response of the functional fibers when exposed to the same concentration of formaldehyde.
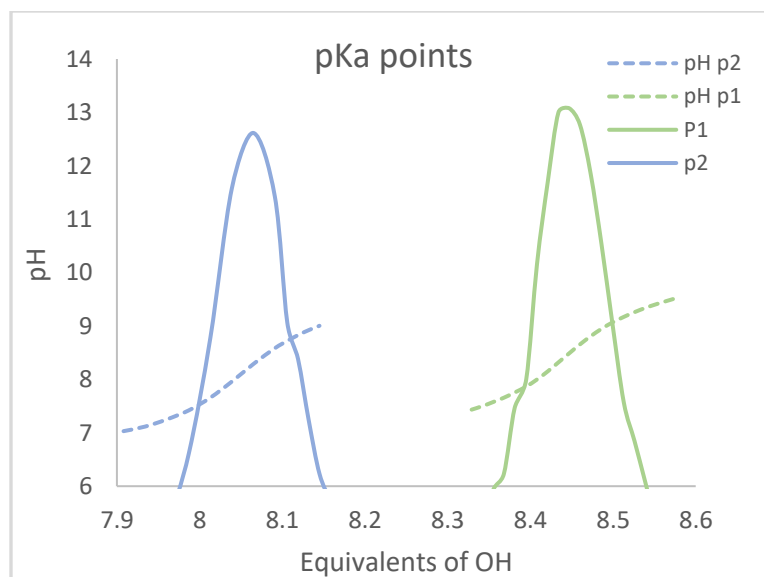
Figure 16. Acid titration of polymers P1 and P2. P1, chitosan. P2, chitosan derivative

Results of color probes survey

The results of the color probes survey showed the different colors that can be achieved depending on the pH of the solution, in the Figure 17, a range of 6 colors is shown in principle, this range makes it possible to observe a more detailed color change, in the same way C3 shows a change, which although the range is smaller, is still good for color change analysis, for C3, the most significant change occurs at pH 9 to 10 where the intense red color is almost transparent, this range being where it is more viable to work. Due to the results, it was decided to work in three ranges, pH4 pH7 and pH10, as the %CC was more significative at these pH values.

Quantification color change based on pH

As is shown in the Figure 17, the colors in solutions CP1, CP2 and CP3 show us a range of colors with which we can work on the color change, this is given with respect to the modified pH.

CP1

CP2

CP3
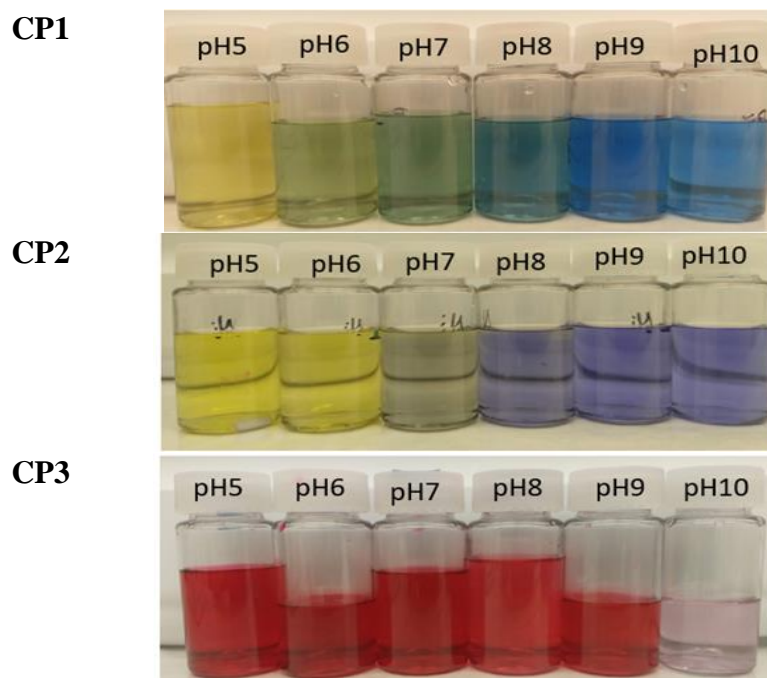
Figure 17. Range of colors reached at different pH for
C1, CP2 & CP3

UV-vis results of pH4

The plots shared below (Figure 18 - Figure 23) show the change of the absorbance measured in a UV-vis spectrophotometer at the different formaldehyde concentrations. The different absorbance is due to the change on the concentration of FA, which makes the pH goes to acid side, and the interactions between the different color probe and FA.
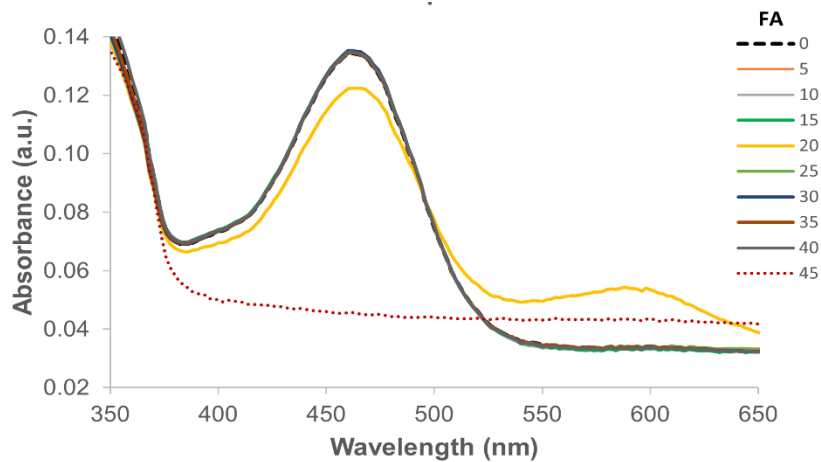
Figure 18. Plot for Ni - pH4
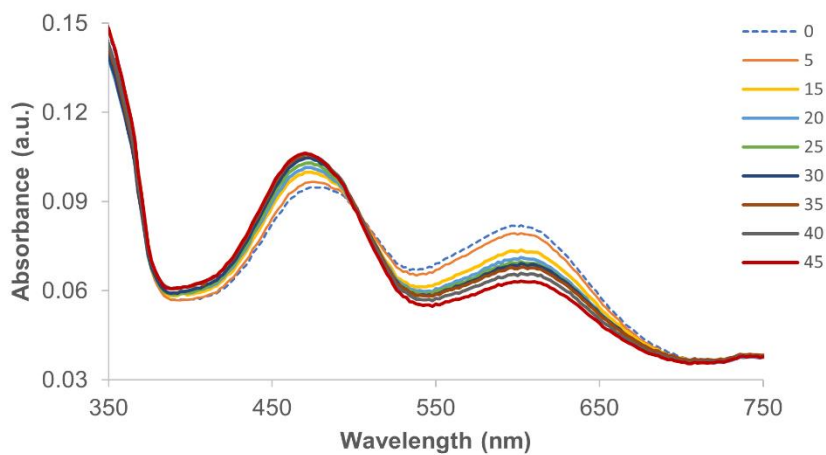
Figure 19. Plot for NiP1 – pH4
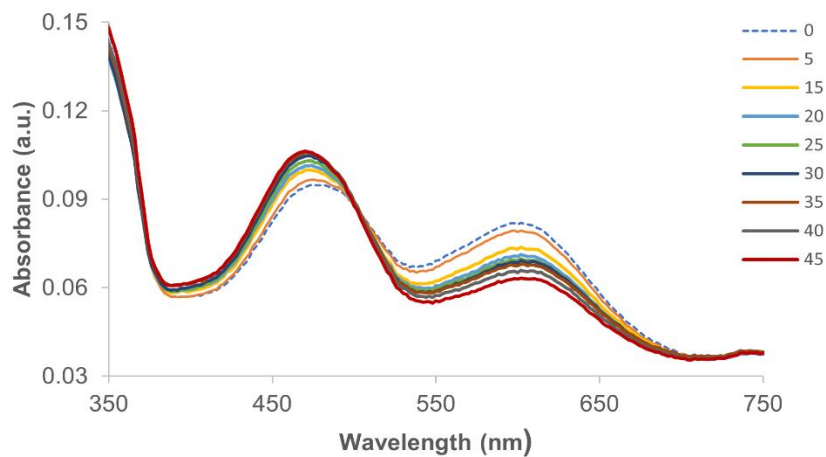
Figure 20. Plot for Ni P2 – pH4
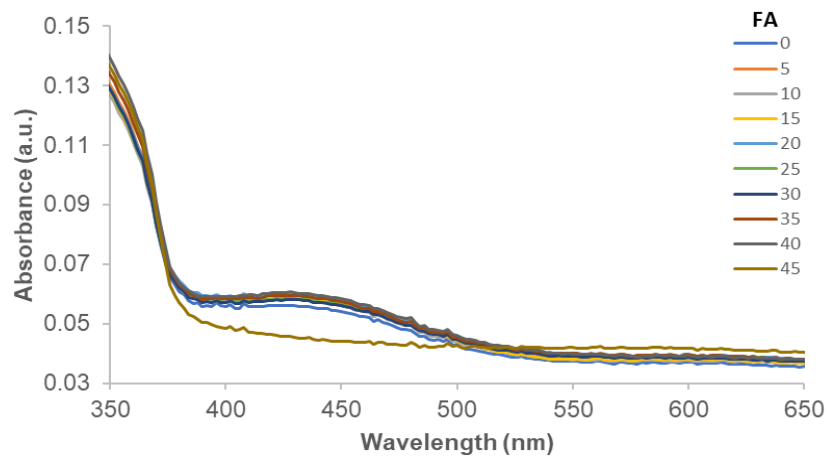
Figure 21. Plot for Bx – pH4
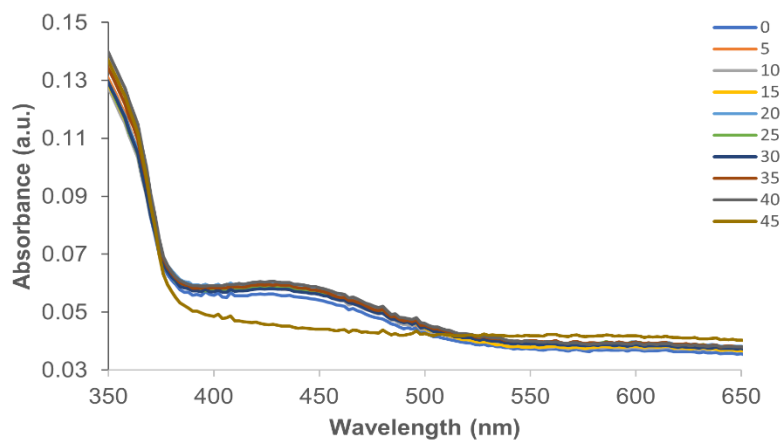
Figure 22. Plot for BxP1 - pH4
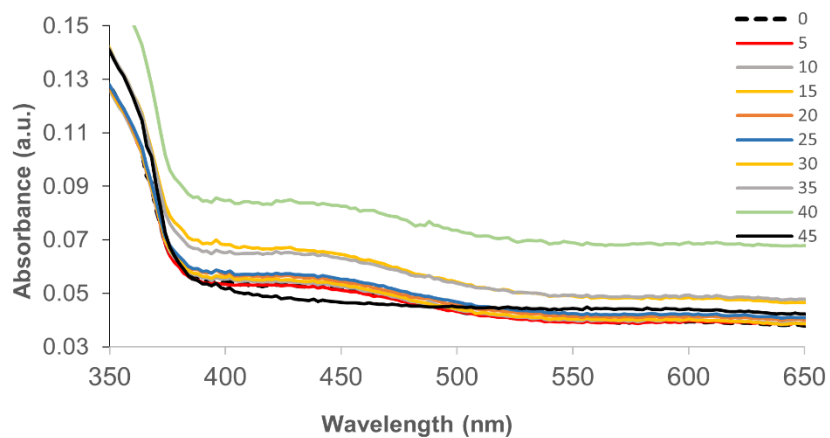
Figure 23. Plot for BX – P2 pH4

Quantification of %CC based on formaldehyde content and pH value

Results obtained using microwell plates and three different color probes (bromoxylenol blue CP1, nitrazine yellow CP2, and bromocresol purple CP3) are shown here. Images of microwell plates using color probes combined with Polymer 1 (P1) and Polymer (P2). As shown in the images in Figure 24, the effect of using P1 and P2 improves the sensitivity for detection in color change at lower levels of formaldehyde concentration. Likewise, it is possible to expand the range of working pH values since the same color probe developed a very different range of colors at the different pH values. In the experiment in the microwell plate containing CP3 alone, the significant changes occurred at higher FA values, contrary to low values where the change was almost zero. In the presence of P1 or P2, the color probe showed a color change at low formaldehyde concentration at neutral and alkaline pH (from clear to red color). Although this color change would be helpful for the colorimetric test, CP3 because of this, CP3 was not used for the mPAD experiments as the performance of the color probe on the paper was significantly different compared to its performance in solution. The color probes CP1 and CP2 showed similar performance in the mPADs and the color probes, with a wide range of colorimetric changes.

The esponse to different formaldehyde concentrations in the different systems constituted by three different color probes (C1-C3), with or without adding polymer P1 or polymer P2, at different pHs. C1, nitrazine yellow. C2, Bromocresol Purple, C3, Pararosalinine chloride. P1, chitosan. P2, chitosan derivative. As it was described in Figure 12, the pH value on each row is constant and increases from bottom to top rows, and the concentration of FA is the same on each column and increases from right to left columns (Figure 24)
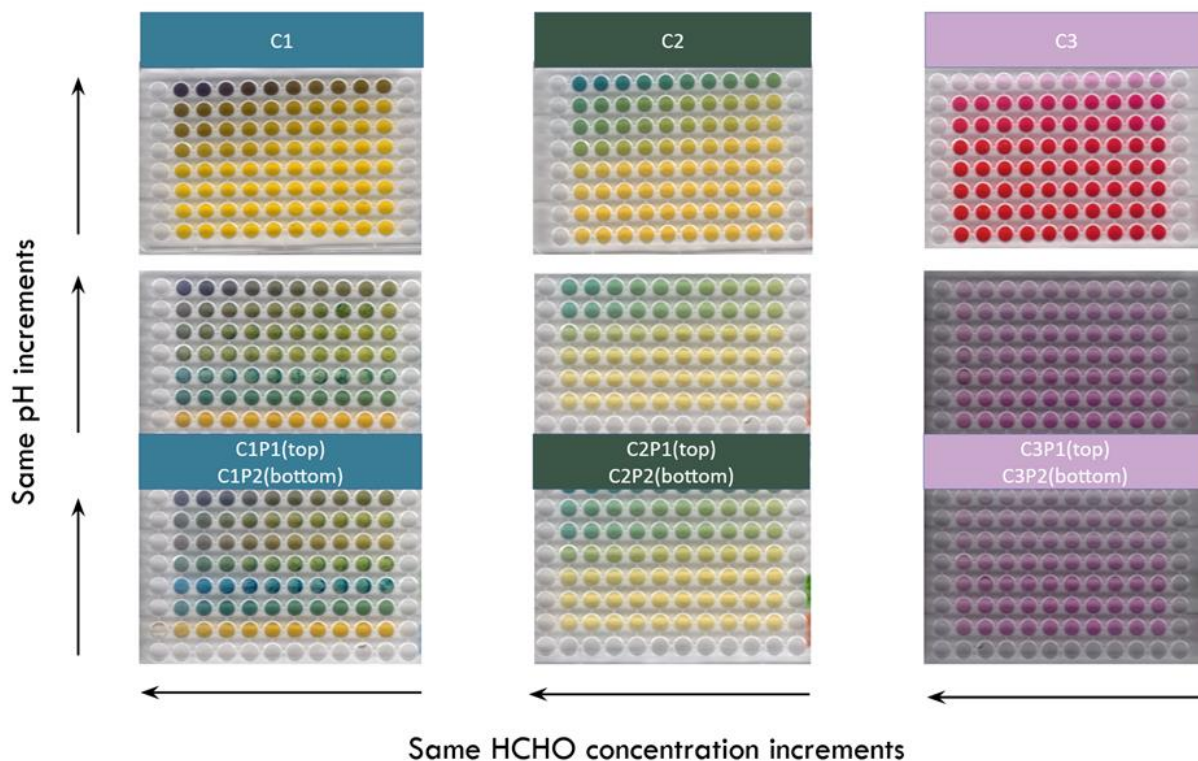
Figure 24. Response of the systems, constituted by the same concentration of color probe Cx and polymer Px to different formaldehyde concentrations, at different pH values.

Characteristics of developed PADs

Paper sheets were prepared following the TAPPI T205 sp-02 standard method. As described earlier, three different hand sheets were prepared: PP0, PP1, and PP2. After drying, discs of 6 mm diameter were cut from PP0, PP1, and PP2 and coated with the color probe. The dip-coating method displayed the best results in the distribution of the color probe, and therefore it was selected for preparing the individual PADs. The picture of the samples selected for the mPAD is shared in Figure 24. The PADs CP1.10 and CP2.7 were prepared with the sample PP1, and the PADs CP1.7, CP2.4, CP2.10, and CP2.4 were prepared with the sample PP2.

Selected coating method. The automatic thick film and the spray method showed areas where a higher concentration of the polymer is observed. The uneven distribution occurs because the polymer of absorbs and dry quickly when it meets the paper. As a result, the color is not completely uniform (Figure 25). A better distribution of the dye was observed with the dip coating technique (Figure 26). For that reason, the dip coating technique was used for the preparation of the sensor constituted by six individual PADs (A-E).
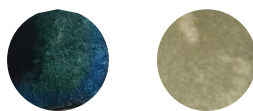
Figure 25. Color distribution using spray (left) and thick film (right)

Our formaldehyde sensors were exposed to different concentrations of formaldehyde (0.05 to 0.08 ppm), based on the FA threshold values established by the different regulatory agencies. In the color analysis, using FIJI software, measuring the percentages of change of R, G and B, vary from one sample to another, being in the red area where the greatest changes are shown, this due to the range of colors of the PAD's with which we work. By having the color changes at different concentrations and color probes called A, B, C, D, E & F (Figure 26) having this, it is possible to obtain a color chart and with this make a direct comparison in terms of formaldehyde concentration to which it was exposed, the difference in the pH of each one and thus be able to see the clearly the changes in color. A greater range of comparison between the PADs used it is possible to have a more specific reading
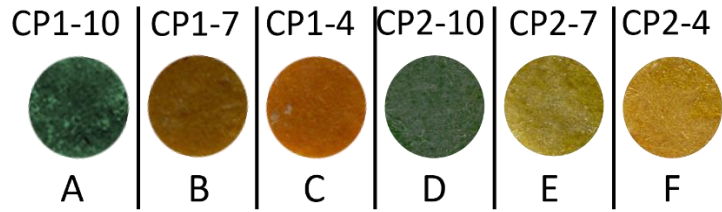
Figure 26. Surface modified aspect of the PADs

Results of standard error for RGB

The results show a variation within the range, the error may be due to the characteristics of the paper where the fibers may be more concentrated in certain areas and thus have more color absorption.
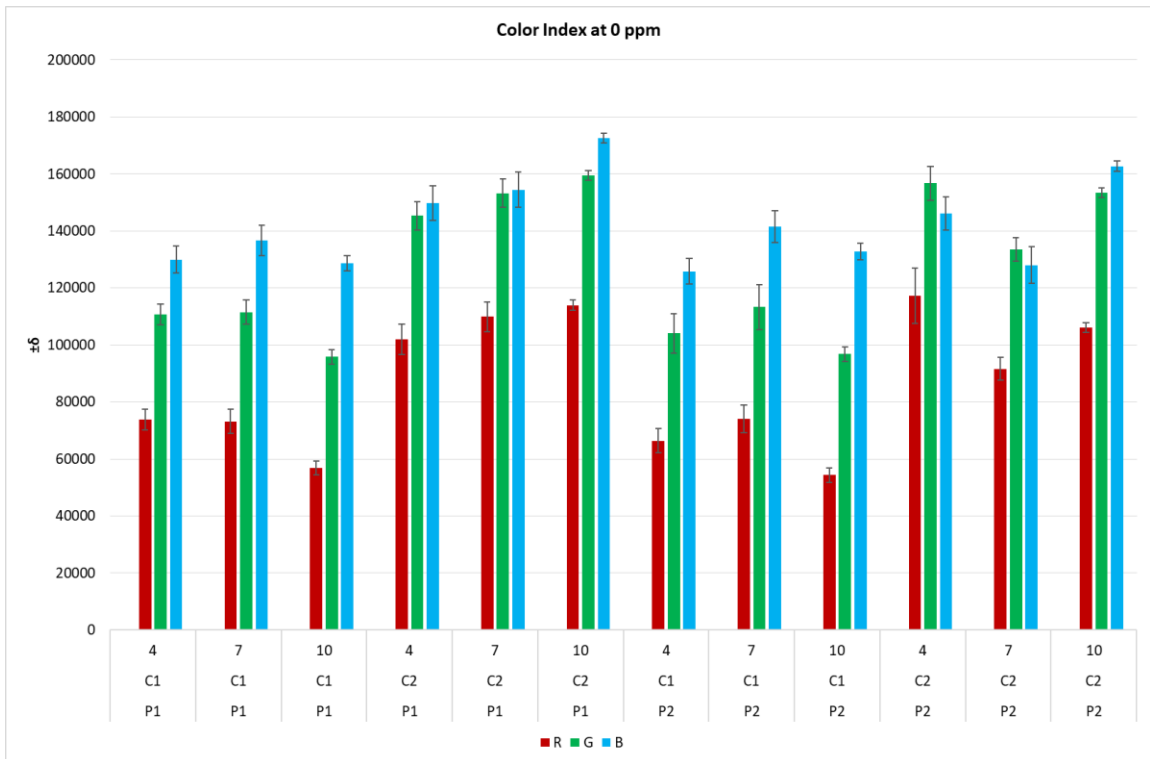
Figure 27. standard error for the PAD's at 0ppm

Response of PADs to exposure to formaldehyde

Based on the thresholds of different regulatory agencies, the PADs were exposed to different concentrations of formaldehyde (0.05 to 0.08 ppm). with this, significant changes in colors were obtained, even at low concentrations. In the color analysis, using FIJI software, measuring the percentages of change of R, G and B, vary from one sample to another, being in the red area where the greatest changes are shown, this due to the range of colors of the PAD's with which we work. By having the color changes at different concentrations and color probes, it is possible to obtain a color chart and with this make a direct comparison in terms of formaldehyde concentration to which it was exposed, the difference in the pH of each one and thus be able to see the clearly the changes in color. A greater range of comparison between the PADs used it is possible to have a more specific reading.

A combination of 6 individual PADs was exposed to different concentrations of formaldehyde in a small stainless-steel chamber calibrated with a protocol adapted from ASTM D6007-14. At the end of one hour of exposure, the PDSs were scanned. This image can be used as a color chart to measure the formaldehyde content of an unknown sample that emits formaldehyde. The percentage of color change was calculated using the Fiji software. The percent change in R, G, or B values, before and after exposure to formaldehyde (ie, at 0 ppm, and the concentration of the target formaldehyde level) is shown in the Figure 29. At the same time, the electronic sensor device showed different results depending on the concentration of formaldehyde (Figure 28), readings at 0.05 ppm shows a spike at the firsts 5 min, then the concentration drops. Even the spike occurs very quickly, our paper-based sensors were tested during 60 min as described in the ASTM D6007-14 standard, because only the total amount of formaldehyde matters for the measurement and the distribution along the time should not affect the result. It is important to point out that the plots at

very low concentrations were not consistent, which was attributed to the lower detection limit of the electronic device. However, significant changes in colors were observed in the FA concentration mentioned before, even at very low concentrations, which serves a good indication that our system performs better even at very low concentrations of FA.
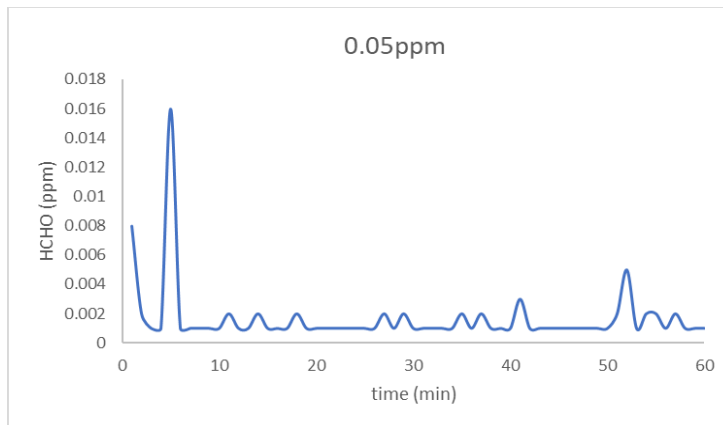
**Figure 28**. Plot for the electronic sensor after exposed to formaldehyde inside the chamber

Color chart of the PAD's

ppm	0	0.05	0.06	0.07	0.08
A					
B					
C					
D					
E					
F					

Figure 29. Color chart with the difference in the formaldehyde exposed PADs

As can be seen in Figure 29, the color change is evident from 0ppm to 0.08ppm concentration, the color changes are similar to those shown in the color change tests in solution, where the change towards the acid side shows a color with a tendency to yellow when the FA concentration is higher.
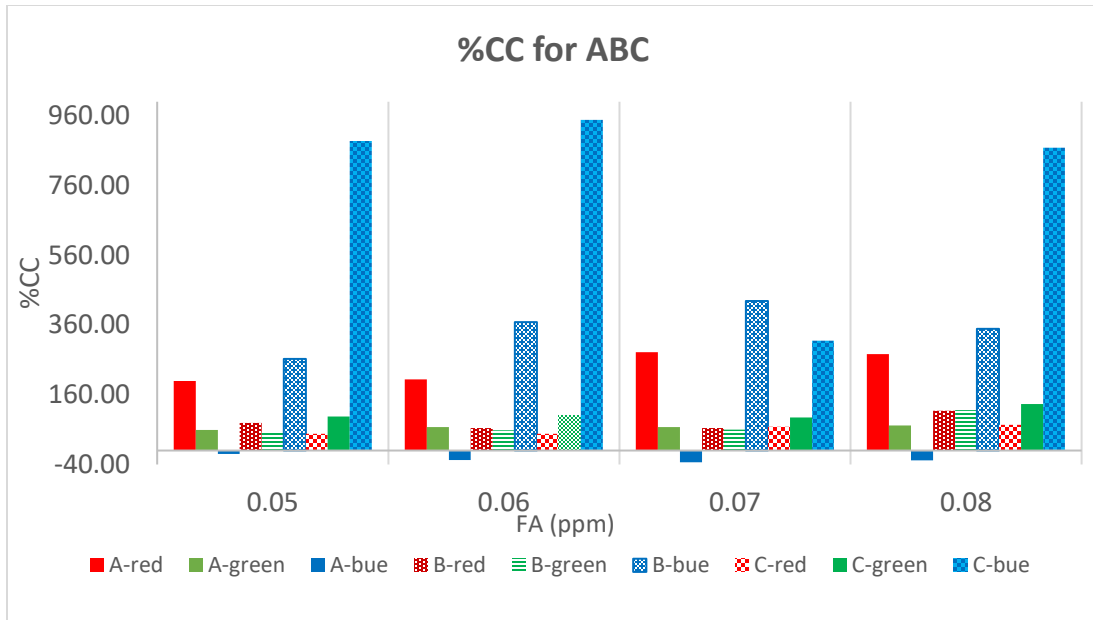
Figure 30. %CC for ABC where the bigger change in color is in blue
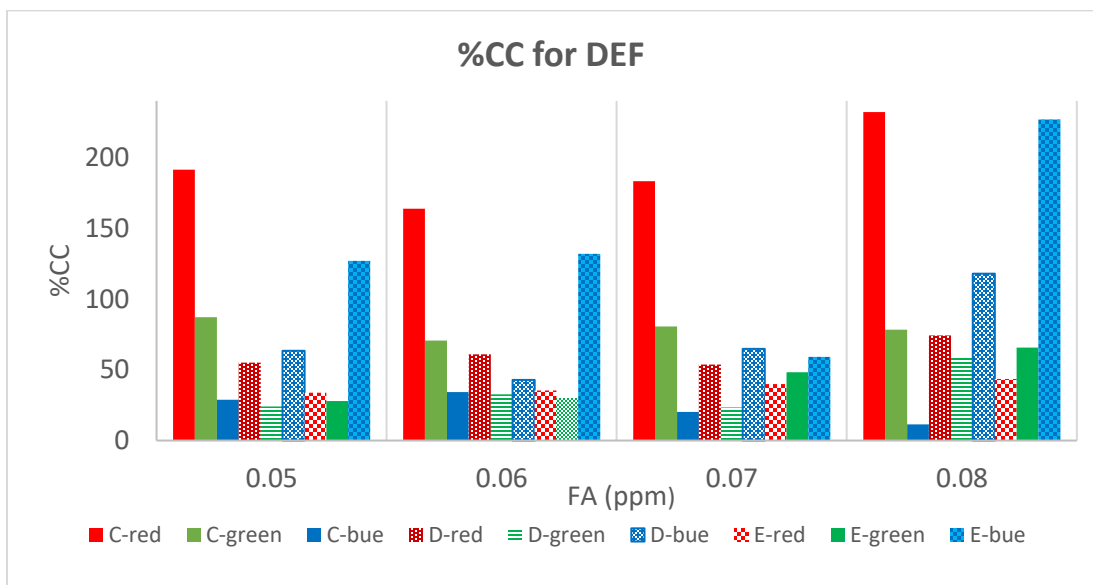
Figure 31. %CC for DEF where the bigger change is in RED

The graphs in Figure 30 and 31, clearly show the different responses in each PAD to the different formaldehyde concentration. Furthermore, the relative variation between R, G and B is not the same. For example, the DEF individual PADs show the most significant percentage of red color

change, whereas the ABC showed a more preponderant change of the blue color. The results are in agreement with the results observed during the microplate tests.
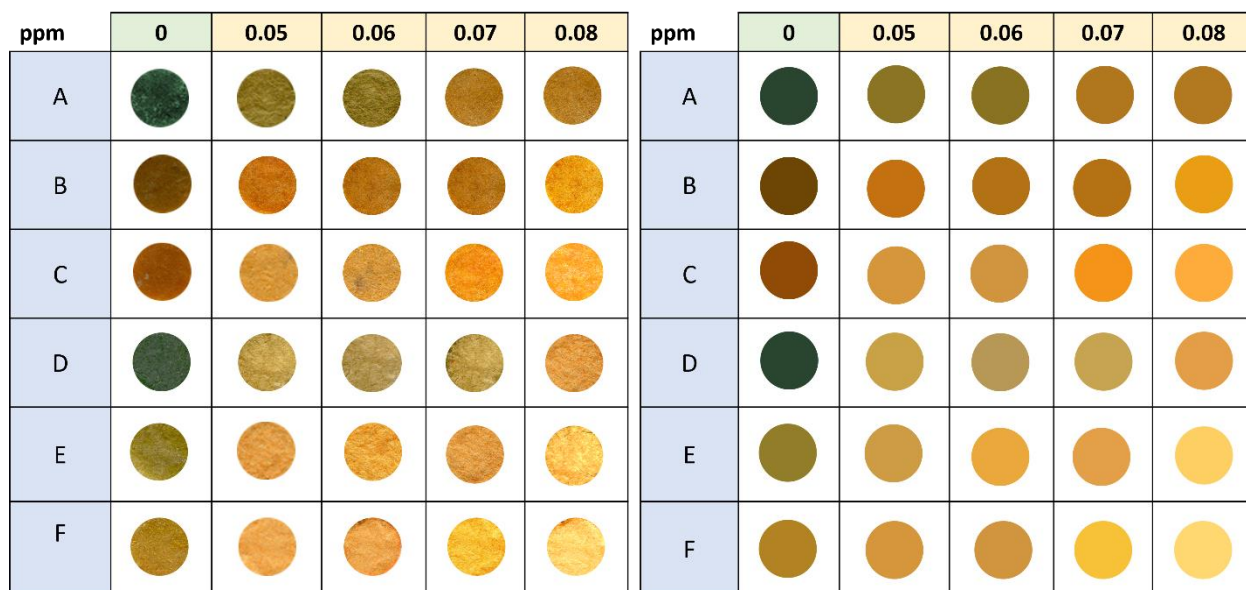
Conversion of the change from RGB to HEX

The change to HEX code helps us to observe in a clearer way the color change in the chart, besides this the code gives us a better way to have knowledge of the color shown and with this is possible to demonstrate that the RGB color measurements are accurate, it is also possible with the codes to develop a mobile application for future work, with this tool it will be possible to understand the changes for people with visual color problems and to do it in a faster and more accurate way.

The chart of HEX code colors helps us to observe in a clearer way the color change in the chart, besides this the code gives us a better way to have knowledge of the color shown and with this is possible to demonstrate that the RGB color measurements are accurate, it is also possible with the codes to develop a mobile application for future work, with this tool it will be possible to understand the changes for color-blind and visually Impaired people, and to do it in a faster and more accurate way.

Table 6. Conversion of RGB values to HEX

FA	CP1.(pH)	R	G	B	HEX	COLOUR	FA	CP2.(pH)	R	G	B	HEX	COLOUR
0ppm	CP1.10	41.66	69.42	47.9	29452F		0ppm	CP2.10	38	60.5	31.14	29452F	
	CP1.7	109.6	70.07	6.63	6D4606			CP2.7	103	86.4	21.24	6D4606	
	CP1.4	144.6	76.07	6.6	904C06			CP2.4	143	124	38.71	904C06	
0.05ppm	CP1.10	139.2	116.4	36.5	8B7424		0.05ppm	CP2.10	195	161	77.82	8B7424	
	CP1.7	205.6	156.1	68.6	CD9C44			CP2.7	227	157	70.19	CD9C44	
	CP1.4	214.1	150.7	59	D6963B			CP2.4	233	168	80.4	D6963B	
0.06ppm	CP1.10	137.7	114.4	34.4	897222		0.06ppm	CP2.10	181	150	84.15	897222	
	CP1.7	180.6	114.5	22.1	B47216			CP2.7	234	165	58.74	B47216	
	CP1.4	210.4	149.9	63.5	D2953F			CP2.4	239	168	79.95	D2953F	
0.07ppm	CP1.10	176.7	119.9	31.7	B0771F		0.07ppm	CP2.10	194	160	76.72	B0771F	
	CP1.7	180.7	114.3	21.8	B47215			CP2.7	225	156	69.68	B47215	
	CP1.4	244.4	148.6	25.9	F49419			CP2.4	249	194	56.16	F49419	
0.08ppm	CP1.10	178.7	121.8	33.7	B27921		0.08ppm	CP2.10	226	156	68.8	B27921	
	CP1.7	234.9	158.7	22.4	EA9E16			CP2.7	250	199	89.84	EA9E16	
	CP1.4	255	173	61.3	FEAD3D			CP2.4	255	215	112.38	FEAD3D	

Sets of 6 individual PADs (rows A-E, column "0" ppm) were exposed to different concentrations of formaldehyde. The unique combination of colors developed on each set, after 1h exposure to formaldehyde is shown in the ***color chart*** below (column 0.05-0.08 ppm). After image analysis, RGB values from each PAD can be converted into HEX values.

The **HEX values chart** showed on the right of the image below can be printed and used for the determination of formaldehyde emissions from unknown samples. Moreover, the formaldehyde emission levels can be calculated by a software using unexpensive colorimeters for determining the HEX values (impaired vision people still can use our system)

ppm	0	0.05	0.06	0.07	0.08	ppm	0	0.05	0.06	0.07	0.08
A						A					
B						B					
C						C					
D						D					
E						E					
F						F					

Figure 32. Comparison between color chart and HEX chart

Curve fitting for the determination of FA in air using our FA sensor

The plots made using Origin2018-95E (Figure 33) show the change on each RGB values, at the different concentrations (dot markers) and the trends or spline observed for each individual PAD. When using the spline is possible to obtain a smoother curve. Using a second order polynomial fit of the spline, it is possible to obtain simple equations for the determination of the FA concentration of an unknown sample.
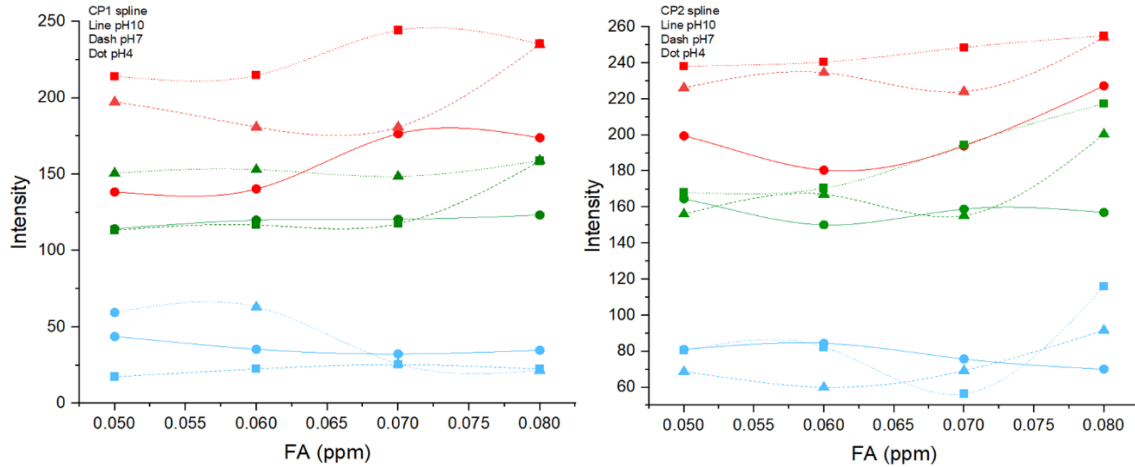
Figure 33. Splines for CP1 and CP2

Example of determination of RGB for chart A

For example, three different equations describing the color intensity change observed in the disc

A exposed to different FA concentrations were obtained after the curve fitting of the splines

showed in Figure 33 (Eq.6)

Red equation: $y_R = -12402x^2 + 3562.4x - 20.333$ (Eq.6)

Green equation: $y_G = -7454x^2 + 1191.2x + 74.53$ (Eq.6)

Blue equation: $y_B = 28918x^2 - 4066.7x + 175.37$ (Eq.6)

were y_i is the intensity of the *i* color in the RGB system, and x is the FA concentration.

The change of x for the predicted concentration of FA could be substituted for a concentration to

get the RGB values and then, get the HEX for the new color.

Prediction of color for 0.075 ppm

Having the equations obtained with the splines and substituting the values of x by the desired

concentration, it is possible to obtain the RGB value for each PAD and with this create a color by

converting the values to HEX. Figure 34 shows the concentration at 0.075 ppm and how the colors follow the color trend.

Figure 34. Results of predicted values at 0.075 ppm

Conclusions

As evidenced from the results, different color probes can be used for a colorimetric detection method of the formaldehyde concentration in air. The different color probes can show the surface pH change that occurs on the surface of a paper decorated with natural polysaccharides and polysaccharide derivatives, which are used to improve the sensitivity of the colorimetric method. The different color probes and polymers enabled the fabrication of each individual paper-based analytical device referred to as PAD. Because of the different response on each individual PAD to the same formaldehyde concentration, the utilization of a set of individual PADs for the fabrication of a multi-PAD systems can help lower the detection limit of the analysis. In comparison to the individual PADs, a unique combination of colors developed on the multi-PADs after exposure to formaldehyde allows to distinguish the correct concentration value on the color chart easily, even at very low concentrations of formaldehyde.

This tool might bring a rapid, selective, easy to use, cost-efficient alternative to the existing analytical methods used every day to ensure the safety of the forest products that use formaldehyde during the manufacturing process, and therefore, might contribute to the occupational safety & health safety & health in forest products that use formaldehyde during its manufacturing process.

Bibliography

1.   Pappas G, Herbert R, Henderson W, Koenig J, Stover B, Barnhart S. The Respiratory
        Effects of Volatile Organic Compounds. Int J Occup Environ Health. 2000 Jan 1;6:1–8.

2.   Ferro FS, Silva DAL, Rocco Lahr FA, Argenton M, González-García S. Environmental
        aspects of oriented strand boards production. A Brazilian case study. Journal of Cleaner
        Production. 2018 May 10;183:710–9.

3.   Makowski M, Ohlmeyer M, Meier D. Long-term development of VOC emissions from
        OSB after hot-pressing. Holzforschung. 2005 Sep 1;59:519–23.

4.   Wiegner K, Wilke O, Jann O, Brödner D, Scheffer H, Kalus S, et al. Study on VOC-
        emissions from Oriented Strand Boards (OSB). 9th International Conference and
        Exhibition - Healthy Buildings 2009, HB 2009. 2009.

5.   Mcginnis GD. final project report reducing voc press emissions from oriented strand
        board (OSB) manufacturing (DE-FC07-97IDI3546). In 2002.

6.   IARC. A Review of Human Carcinogens: Vol. F, Chemical agents and related
        occupations. 100F ed. Lyopn, France: International Agency for Research on Cancer; 2012.
        401–446 p.

7.   Kowalczyk P, Miyawaki J, Azuma Y, Yoon SH, Nakabayashi K, Gauden PA, et al.
        Molecular simulation aided nanoporous carbon design for highly efficient low-
        concentrated formaldehyde capture. Carbon N Y. 2017 Nov 1;124:152–60.

8.   Debra A. Kaden, Corinne Mandin, Gunnar D. Nielsen and PW. WHO guidelines for
        indoor air quality: selected pollutants. Copenhagen Ø, Denmark: World Health
        Organization; 2010. 103–142 p.

9.   ATSDR. Department of Health and Human Services. Public Health Agency for Toxic

        Substances and Disease. 2008. p. 1–12.

10.   Noor Aini B, Siddiquee S, Ampon K. Development of Formaldehyde Biosensor for

        Determination of Formalin in Fish Samples; Malabar Red Snapper (Lutjanus malabaricus)

        and Longtail Tuna (Thunnus tonggol). Biosensors (Basel) [Internet]. 2016;6(3). Available

        from: https://www.mdpi.com/2079-6374/6/3/32

11.   Marilyn B. Formaldehyde Update-Prepared for the WHO Children's Health Committee-

        2012-Some Updates 2013. 2013.

12.   Liu Y, Yang H, Ma C, Luo S, Xu M, Wu Z, et al. Luminescent Transparent Wood Based

        on Lignin-Derived Carbon Dots as a Building Material for Dual-Channel, Real-Time, and

        Visual Detection of Formaldehyde Gas. ACS Applied Materials & amp; Interfaces. 2020

        Jul 14;12(32):36628–38.

13.   Swenberg JA, Moeller BC, Lu K, Rager JE, Fry RC, Starr TB. Formaldehyde

        Carcinogenicity Research: 30 Years and Counting for Mode of Action, Epidemiology, and

        Cancer Risk Assessment.

14.   Salthammer T, Mentese S, Marutzky R. Formaldehyde in the Indoor Environment.

        Chemical Reviews [Internet]. 2010 Apr 14;110(4):2536–72. Available from:

        https://doi.org/10.1021/cr800399g

15.   Musto CJ, Suslick KS. Differential sensing of sugars by colorimetric arrays. Current

        Opinion in Chemical Biology. 2010 Dec 1;14(6):758–66.

16.   Herschkovitz Y, Eshkenazi I, Campbell CE, Rishpon J. An electrochemical biosensor for

        formaldehyde. Journal of Electroanalytical Chemistry. 2000 Sep 8;491(1–2):182–7.

17. Mati-Baouche N, Elchinger PH, de Baynast H, Pierre G, Delattre C, Michaud P. Chitosan as an adhesive. European Polymer Journal. 2014 Nov 1;60:198–212.

18. Boroumand H, Badie F, Mazaheri S, Seyedi ZS, Nahand JS, Nejati M, et al. Chitosan-Based Nanoparticles Against Viral Infections. Frontiers in Cellular and Infection Microbiology. 2021;11(March):1–22.

19. Pohl M, Michaelis N, Meister F, Heinze T. Biofunctional Surfaces Based on Dendronized Cellulose. Biomacromolecules [Internet]. 2009 Feb 9;10(2):382–9. Available from: https://doi.org/10.1021/bm801149u

20. Adam Dimech. RGB to HEX in Excel [Internet]. Adam Dimech's Coding Blog. 2016. Available from: https://code.adonline.id.au/rgb-to-hex-in-excel/