# DETERMINATION AND ASSESSMENT OF FORMALDEHYDE RELEASE FROM WOOD–BASED PANEL

*Đến tòa soạn 11 - 12 - 2015*

**Cao Thị Thúy Hải, Tạ Thị Thảo**
*Khoa Hóa học - Trường Đại học Khoa học Tự nhiên - Đại học Quốc gia Hà Nội*

## TÓM TẮT

## XÁC ĐỊNH VÀ ĐÁNH GIÁ HÀM LƯỢNG FOMANDEHIT PHÁT TÁN TRONG VÁN GỖ NHÂN TẠO

*Một số mẫu ván gỗ nhân tạo MDF và PW đã được thu thập tại một số xưởng sản xuất và cửa hàng đồ gỗ nội thất ở Hà Nội để đánh giá lượng fomandehit phát tán. Hàm lượng fomandehit trong dung dịch hấp thụ được xác định bằng phương pháp phân tích quang phổ hấp thụ phân tử UV-ViS với hỗn hợp thuốc thử acetylaxeton và amoni axetat. Giới hạn phát hiện của fomandehit trong dung dịch là 0,3 ppm và khoảng tuyến tính từ 1,0 đến 10,0 ppm. Với cùng loại vật liệu, khi tăng nhiệt độ của môi trường thí nghiệm lên 5$^o$C thì mức độ phát tán fomandehit tăng từ 1,2 đến 2,2 lần. Ở 50$^o$C, hàm lượng fomandehit phát tán từ mẫu MDF và PW lần lượt là 1,327 và 0,752 mg/100g vật liệu, đều thấp hơn so với mức hàm lượng yêu cầu quy định tại QCVN 16: 2011/BXD.*

## 1. INTRODUCTION

Formaldehyde, an economically important chemical, is classified as a human carcinogen that causes nasopharyngeal cancer and probably leukemia [4]. The International Agency for Research on Cancer (WHO), reclassified formaldehyde from "probably carcinogenic to humans (Group 2A)" to "carcinogenic to humans (Group1)" in June 2004 [2].

In today's society, many building materials emit volatile organic compounds (VOCs) which have the potential to affect health [3]. Formaldehyde is the main VOC released from pressed-wood products used in home construction, including

products made with ureaformaldehyde resins. Wood-based panel products (WBPs) become increasingly specialized in recent years and used in wide ranging application especially indoor environment. The formaldehyde emitted from these panels has become one of the major causes of degrading indoor air quality, which can negatively affect human health and productivity.

Wood based panels often are divided into three main types. The most popular WBP in Vietnam is medium density fiberboard (MDF)-a versatile wood-based panel with good machinability. MDF is used mainly for the furniture industry, skirting boards, architraves, packaging material, in the door industry. Secondly, it is particle board (PB) known as chipboard. It is a multi-purpose material and one of the most widely-used wood-based panels. The last one, plywood (PW) is manufactured to meet stringent requirements for exterior application.

In Vietnam, the standard of formaldehyde content depends on each type of wood-base panel products. For PW, MDF, PB, the level requirement for the content of formaldehyde is lower than 8 mg, 9 mg, 8 mg per 100 g sample, respectively [7].

In order to control the formaldehyde emission, many different methods have been used to measure the formaldehyde emission from WBPs. The perforator method EN 120 was popularly used in Europe. While the desiccator test was developed in the middle of the 1970s in Japan and standardized in the United States in 1983 and became standard method in North America, Australia and Asia. In addition, other methods such as test chamber method EN 717-1, gas analysis method EN 717-2 and FLEC method also have been used for the determination of formaldehyde emission. Each approach is suitable for requirement of each product [5,8].

In this study, since these methods are very complicated. They require loads of expensive apparatuses like test chamber, air sampling system, gas analysis test equipment or extraction apparatus…Therefore, formaldehyde emission from wood-based panel was determined by flask method-a particularly simple approach, following European Standard EN 717-3 [6].

## 2. EXPERIMENTAL

### 2.1. Chemicals and reagents

All reagents were prepared by analytical grade chemicals and distilled water. Formaldehyde stock solution was titrated by mixing formaldehyde standard solution with iodine solution and sodium hydroxide solution. After 15 minutes standing protected from light add sulfuric acid solution. Titrate back the excess iodine with the sodium thiosulfate solution. Near the end of the

titration add some drops of the starch solution as an indicator.

A 0.037 M acetylacetone solution was prepared by adding 1.00 mL acetylacetone 95% to a 250 mL volumetric flask and made up to the mark with distilled water.

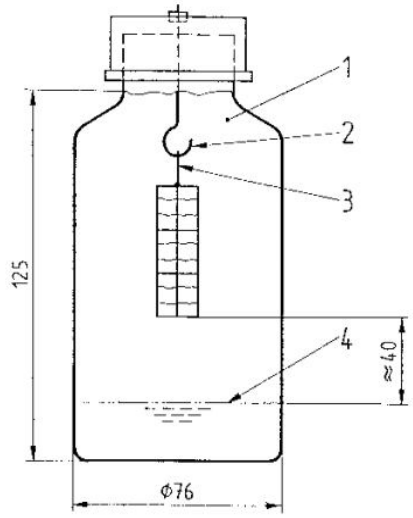
Ammonium acetate solution 2.597M was prepared by dissolving 20 g ammonium acetate in a 100 mL distilled water.

**2.2. Materials**

A WBP samples of MDF was collected from a manufacturing facility in Linh Nam market, Hoang Mai district, Hanoi. A PW samples were obtained from a wood storage shed in Gia Lam district and a wood store on De La Thanh street, Dong Da district, Hanoi. These samples are excess parts in the process of manufacturing funiture. In laboratory, samples were cut into 2cm × 5cm species and storage at room temperature.

**2.3. Apparatus**

The apparatus used to study the formaldehyde emission was shown in Figure 1. It is a 500 mL polypropylene or polyethylene flask-container with tightly lid of the same material and a hookout of stainless steel [6].




1 500 ml polyethylene bottle with bottle top
2 Hook out of stainless steel
3 Elastic rubber band
4 Surface of water

*Figure 1: Test apparatus for the flask method*

The absorbance of complex in this study was measured by the UV-Visible Spectrophotometer 1650 PC (Shi madzu, Japan) with quartz cuvettes.

**2.4. Procedures**

***2.4.1 Determination of formaldehyde emission***

The moisture content of wood-based panels was measured according to European Standard EN 322-1993[1].

The determination of formaldehyde release was based on duplicate sets of test pieces. The individual values shall only differ from each other by a maximum of 20% related to the higher of two single values. Otherwise a third determination shall be carried out [6].

Conect the test pieces with a rubber band as shown in Figure 1. Add 50 mL of distilled water at 20$^{o}$C to the container, attach the lid with the

suspended test pieces and close the container so that it is completely airtight. The bottom surfaces of the test pieces should be approximately 40 mm above the surface of the water. A second container shall be prepared in the same way.

Insert the closed containers into the oven at a temperature of (40±1)$^{o}$C. This temperature shall be maintained throughout the whole test period. The containers shall occupy less than 10% of the whole volume of the oven in order to avoid fluctuation in the temperature. After (180±1) min remove the containers from the oven and immediately take off the lids with the test pieces attached. Transfer the solution from the containers to each of the two 50 ml flasks, close them tightly and allow the contents to cool at ambient temperature to approximately 20$^{o}$C [6].

***2.4.2 Determination of formaldehyde content in samples***

The method based on Hantzsch reaction in which formaldehyde reacts with ammonium and acetylaceton to born diaxetyldihydrolutidin (DDL). DDL is absorbed maximum at a wavelength of 412.0 nm.

10.00 mL is taken from the aqueous solution and added 10.00 mL acetylacetone solution, 10.00 mL ammonium acetate solution which were prepared above in a 50 ml flask. The flask is stoppered, shaken and warmed for 15 min in a water bath of (40±1)$^{o}$C. The now greenish-yellow solution is cooled to room temperature protected from light (about 1 h). The absorbance of this solution is determined at a wavelength of 412 nm against distilled water using a spectrophotometer. A blank test was made with distilled water

3. RESULTS AND DISCUSSIONS

**3.1. Optimization of experimental conditions for determination of HCHO in solution**

***3.1.1 Effect of time***

Pipet 2.50 ml of 50ppm HCHO calibration solution into a 25ml volumetric flask and add 2.50ml of 2.597 M ammonium acetate solution and 5ml of 0.037 M acetylacetone solution. Immediately, it is took place to measure absorbance. The result is shown in Figure 2. It is clear that the complex is stable at more than 1 hour.

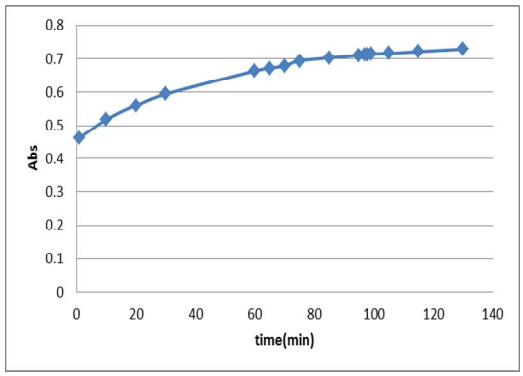



*Figure 2: Effect of time on the making complex reaction of formaldehyde*

### *3.1.2 Effect of ammonium acetate*

The effect of ammonium acetate was tested at 8 levels of ammonium acetate concentration (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 M) and the fixed content of 10.0 ppm HCHO and 0.0074M acetylacetone solution. The result is shown in Table 1.

*Table 1: Effect of ammonium acetate concentration*

| Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| $C_{amoniacetate}$(M) | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 |
| Abs | 0.94 | 1.729 | 2.086 | 2.273 | 2.410 | 2.484 | 2.531 | 2.517 |

### 3.1.3 Effect of acac

To optimization the effect of acetylacetone solution on the making complex reaction, the concentration of ammonium acetate and formaldehyde are fixed ; concentration of acetylacetone changes from 0.00060M to 0.0080M. The result is shown in Figure 2.

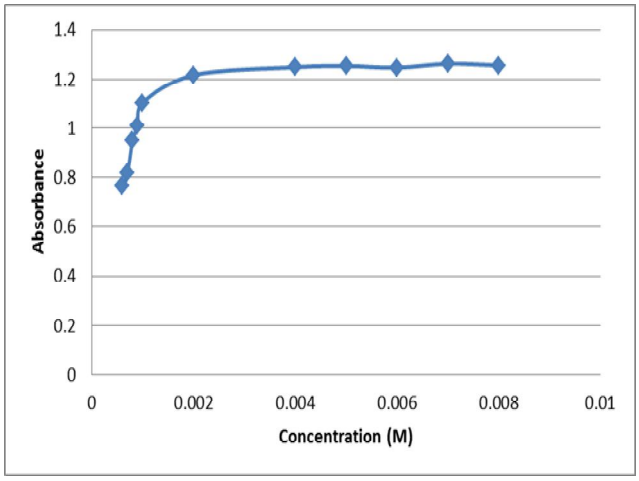



*Figure 3: Effect of acetylacetone concentration*

From the result above, the linear interval of acetylacetone solution is from 0.002 M. It means that with concentration of acetylacetone more than 0.002 M the stable complex was form.

To conclude, the stable complex was formed in the following conditions: concentration of acetylacetone is 0.002 M; concentration of ammonium acetate is 0.6 M; the period of reaction time is about 60 minutes; the reaction temperature is 40$^{o}$C; the maximum absorbance wavelength is 412 nm.

### *3.1.4 Calibration curve*

The calibration curve was constructed at six levels of formaldehyde concentration (0.2, 0.5, 1.0, 2.0, 5.0, 10.0 ppm). The result of the absorptions is shown in figure 4.

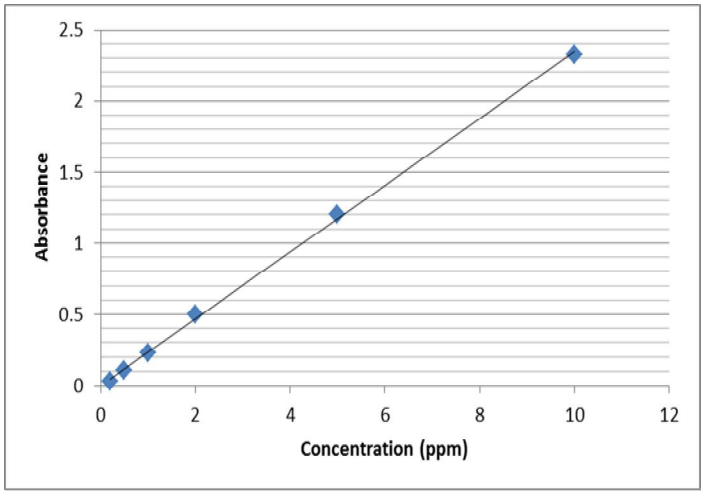



*Figure 4: Calibration curve of formaldehyde*

The equation of calibration curve is:

Abs = 0.0028(±0.0132) + 0.2342(±0.0022).C

Result showed linearity with a good correlation coefficient of 0.9994. The limit of linearity (LOL) was 10 ppm. The limit of detection (LOD) and quantification (LOQ) were 0.3 and 1.0 ppm, respectively, and linear range of this measurement was from 1.0 to 10.0 ppm.

**3.2. The emission of formaldehyde release from wood – based panel**

Figure 4 indicated the values of FE of PW and MDF samples in mg formaldehyde per 100g material measured by EN 717-3 method at two temperature levels of 45$^{o}$C and 50$^{o}$C. Each specimen was tested three times and good repeatability of results was obtained with a maximum relative standard deviation of less than 0.13. It is clear that, the higher temperature, the more emission of formaldehyde from WBPs is. Between 45 (±5)$^{o}$C and 50 (±5)$^{o}$C, the formaldehyde concentration increases significantly from 0.588 to 1.327 mg/100g MDF. In addition, it is obvious that at the same temperature, the formaldehyde content in MDF dramatically decreases when compared with that in PW. However, all the FE values by this study were lower than the E1 standard (<9mg/100g) provided by Vietnam National Technical Regulation on Products, Goods of Buiding Materials (QCVN 16 : 2011/BXD) [7].

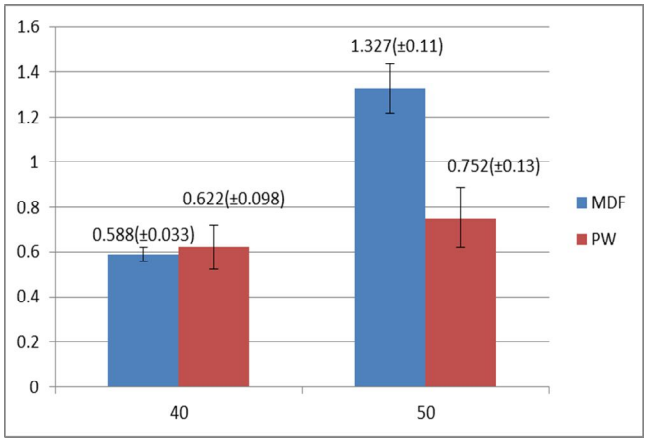



*Figure 4: Formaldehyde emission from different type of WBPs at different temperature ( 45°C and 50°C) measured by EN 717-3 method*

To compare with other methods, figure 5 shows that, although these above samples are measured at high temperature (50°C), the result of formaldehyde emission in MDF is much lower than MDF samples measured by the perforator method EN 120 [2]. There are two main reasons explaining the value of formaldehyde content. The first one being that these samples is stored in manufactures for a long time, since a part of formaldehyde was released. In addition, the flask method EN 717-3 is low sensitivity, thus, the amount of formaldehyde emission are not absorbed completely in aqueous solution.

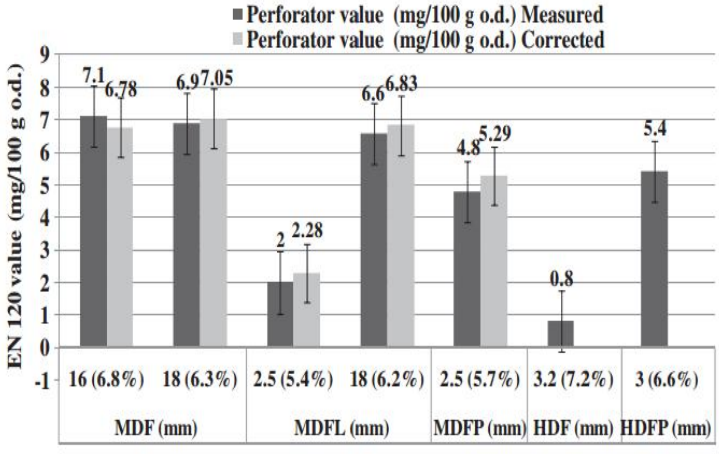



*Figure 5: Measured and corrected values of formaldehyde content from different type of thicknesses of fiberboards measured by EN 120 method (mg/100g). The corrected values at moisture content (MC) of 6.5% The values in parenthesis are the measured moiture content.*

## 4. CONCLUSION

By this study, procedure to determine formaldehyde emission from WBPs was optimized and applied for several kinds of real sample collected from some wood facilities and stores in Hanoi. Formaldehyde was detected in all samples at levels lower than threshold value by QCVN 16:2011/BXD.

*Acknowledgement*

*First and foremost, I would like to thank to my supervisor of this study, Prof. Dr Ta Thi Thao for the valuable guidance and advice. Her willingness to motivate me contributed tremendously to my study. I also would like to thank her for showing me some examples that related to the issue. Besides, I would like to thank the authority of Ha Noi University of Science for providing me with a good environment and facilities to complete this study. Finally, an honorable mention goes to my families and friends for their understandings and supports on me in completing this projectghiên cứu được thực hiện với sự hỗ trợ kinh phí của đề tài TN-14-12.*

## REFERENCE

1. EN 322 February 1993 Wood-based panels - Determination of moisture content.

2. Monhamed Z.M.Salem, Martin Bohm, Jaromir, Jitka Berankova, Evaluation of formaldehyde emission from different types of wood-based panels and flooring materials using different standard test methods, *Building and Environment*, Vol. 49, pp. 86-96, (2012)

3. Sumin Kim, Jin-A Kim, Hyun – Joong Kim, Shin Do Kim, Determination of formaldehyde and TVOC emission factor from wood-based composites by small chamber method, *Polymer Testing*, Vol 25, pp. 605-615 (2006).

4. Ze-li Que, Fei-Bin Wang, Jian-Zhang Li, Takeshi Furuno, Assessment on emission of volatile organic compounds and formaldehyde from building materials, Composites: Part B, Vol. 49, pp. 36-42, (2013).

5. Zohongkai He, Yinping Zhang, Wenjuan, Formaldehyde and VOC emission at diferent manufacturing stages of wood-base panels, *Building and Environment*, Vol. 47, pp. 197-204 (2012).

6. EN 717-3, March 1996, Wood-based panels - Determination of formaldehyde release, Part 3: Formaldehyde release by the flask method

7. QCVN 16:2011/BXD, "Quy chuẩn kĩ thuật quốc gia về sản phẩm, hang hóa vật liệu xây dựng".

8. TCVN 7756-12 : 2007 "Ván gỗ nhân tạo – phương pháp thử", Phần 12: xác định hàm lượng Fomandehit.