A.R.I. Ltd

DETERMINATION OF FORMALDEHYDE EMISSION OF PARTICLEBOARD

Comparison of the methods

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General

Urea-formaldehyde and Melamine-formaldehyde resins are widely used in the manufacturing of particleboard . Their usage is always combined with release of formaldehyde during and after the manufacturing of the boards. Formaldehyde is suspicious to be hazardous to the health , so that it was important to measure the level of the formaldehyde emissions of particleboard . This paper is a presentation of the different methods that were developed to measure the emissions and also includes a comparison of them. Firstly, however, we must say something about the mechanism of formaldehyde release that will help us to better understand the methods of measurement .

Mechanism of formaldehyde release in particleboard.

The free formaldehyde in particle board comes from two sources .

a) The wood itself and

b) The adhesive

The formaldehyde of the wood comes from a combination of mechanical and chemical degradation of wood during the preparation of the flakes and depends a lot on the quality of wood and the intensity of the pre-treatment . The amount of this formaldehyde is generally very low .

The main release of formaldehyde comes from the adhesive :

The reaction between formaldehyde and urea or melamine is an equilibrium-reaction .This means that there will always be some free (unreacted) formaldehyde in a resin , independent of the molar ratio of this resin . Of course in a resin with a low final molar-ratio , the content of unreacted formaldehyde will be lower than in a high molar ratio resin . To achieve a good cross linking in the cured resin (this means good mechanical properties) the resin must have a molar ratio of formaldehyde/urea larger than 1.0 . This means we need formaldehyde in excess . This excessive formaldehyde is in the resin in the form of free (unreacted) formaldehyde and in the form of end standing methylolgroups . A resin contains also other groups which consist of formaldehyde. For example:

-NH-CH_2-NH-	Methylenegroups
-NH-CH_2-O-CH_2-NH-	Methyleneethergroups
-NH-CH_2-O-H	Methylolgroups

Under the conditions by which the resin is cured, all these groups can be hydrolysed and release formaldehyde. The conditions for hydrolysis are : moisture , elevated temperature and acidic environment . Under these conditions the methylolgroups are most unstable ones and the most resistant to hydrolysis are the methylenegroups .

In the surface of the boards, where the temperature is high and the moisture low,we have a fully cured resin with a very high amount of hydrolysis-resistant methylenegroups, while in the core, where the temperature is lower and the moisture high (the water is a retarder), we have more methyleneether and methylolgroups, and therefore a high amount of hydrolysis e.g. formaldehyde release . This means that the free formaldehyde is concentrated in the core of the board. This formaldehyde can be released into the environment and cause problems whichever they are. It is obvious that the formaldehyde has to be released in the environment to be hazardous for the health.

The most accurate method would be therefore to measure the amount of formaldehyde which is released in the environment in order to find out if its concentration in the air exceeds the limits whatever they are. This leads to the large chamber test in which we measure the concentration of the formaldehyde in the air in a closed chamber under constant conditions of air-humidity, temperature and air exchange-ratio. This test is the best simulation to estimate the formaldehyde levels we would have in a room containing furniture made of UF-resin bonded particleboard. This test however takes very long and the apparatus is extremely expensive so that it is not possible for every particleboard plant to possess it. Many different methods were developed to give a fast, easy and accurate estimation of the chamber test for a board . Here is a presentation of these methods .

Methods of determination in particleboard .

We have two different types of methods to determine the emission of formaldehyde :

a) The small scale lab-methods.

b) The chamber methods

The small scale lab-methods.

The different small scale lab-methods are following :

1) The gas analysis methods and

2) The perforator method .

We have two different types of gas analysis methods:

a) The stationary and

b) The dynamic gas analysis.

The stationary methods are:

s.1) The WKI bottle-method

s.2) The modified Roffael method

s.3) The dessiccator method

s.4) The micro diffusion-method

s.5) The SINTEF method

s.6) The FAHRNI method

s.7) The gas analysis chamber of Wittmann

s.8) The TNO gas analysis method

s.9) The jar-method

The dynamic methods are:

d.1) Saug und spalt methode

d.2) The gas analysis-method of Stoeger

d.3) The gas analysis-method of FESYP

The difference between stationary and dynamic methods is following:

In the stationary methods we measure the equilibrium concentration of formaldehyde in the air surrounding the sample but this air is not renewed . In the dynamic methods we measure the concentration of formaldehyde in a constant stream of air blown to the sample .

A special case is the DMC method (developed in the USA) whichdoes : dynamic and stationary measurements .This particular method will be described in a special chapter.

The Perforator method

The Perforator method is the only method where the extraction of the not bonded formaldehyde in the board is performed with a liquid . This method belongs to the dynamic extraction methods since the formaldehyde which is extracted from the wood with the first solvent (the toluene) is continuously removed from it by the means of water so that we could say that the first extraction solvent never reaches an equilibrium point in formaldehyde.

b) The chamber methods

There is one chamber method : The large chamber method . This method is the only one that gives accurate results about the emissions of the board under realistic conditions. This is also the method that is accepted by most countries . However recent developments in the analytical teqnique will possibly lead to a differentiation of the method concerning the volume of the chamber .

Detailed description of the methods

The large chamber method

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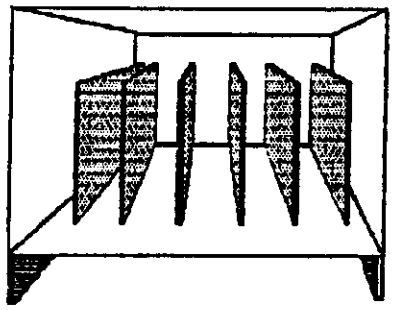

First of all we should see a short description of what is called large chamber . The large chamber is a room of not standard dimensions . The chamber however, has to be large enough to put large board samples in it . The chamber has the possibility of creating standard conditions, such as humidity, temperature, air exchange ratio, etc. In this room we put the board samples (the dimensions of the samples are in the range of 2 meters by 1 meter) and we measure the formaldehyde concentration in the airstream which we blow into the chamber . In the beginning of the test the concentration changes rapidly, but after some time (depending on the test parameters and the samples) the concentration of formaldehyde in the airstream becomes constant and this is the large chamber value of this sample. The detection of formaldehyde is either chemical or electronical.

When boards have to be classified with the large chamber method, then samples with the diimensions 2 meters by 1 meter by thickness are placed in the chamber so that we have a ratio of $1m^3$ of chamber volume for every $1m^2$ of board. The temperature is set to 23 °C ± 0.5 K, the relative air humidity at 45% ± 2% and the air exchange ratio at 1/hr. Normally it takes 60 to 80 hrs for the formaldehyde level to stabilise. The board is classified as E1 when the concentration of formaldehyde in the airstrem is below 0.1 ppm.

There is a correlation between the concentration of formaldehyde and

a) The air exchange ratio in the chamber (hyperbolic)

b) The temperature (linear)

c) The air humidity (linear)

d) The charge (m^2 of board surface / m^3 of chamber) (parabolic)

e) and of course the amount of formaldehyde which is in the board (the equation is specific for each board)

Referring to a). It should be noted that variation of the exchange ratio gives higher concentrations of formaldehyde in the air than expected theoretically. This means that the formaldehyde release of the board increases with the air exchange ratio. And this again means that we have a partial equilibrium at lower air exchange ratios. Berge and the co-workers have done some work on the mechanism of reaching this ***"equilibrium concentration"*** in the chamber . Working at constant humidity and temperature they have developed a mathematical model for the concentration of formaldehyde under these conditions.

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$$C_\infty = \frac{K_g \times \alpha}{n + K_g \times \alpha} \times C^*$$

C_∞ is the "equilibrium"concentration of formaldehyde in the air

Kg is the masstransferconstant

α is the charge factor (m^2 of board surface / m^3 of chamber)

n is the air exchange ratio

C* is the "equilibrium"concentration of formaldehyde when the air exchange is 0

The masstranfercoefficient depends a lot the surface of the board and explains the change of the emissions of a board in case of laminating,coating etc.

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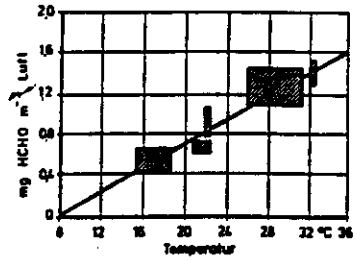

We can see the linear correlation between large chamber values and the temperature.

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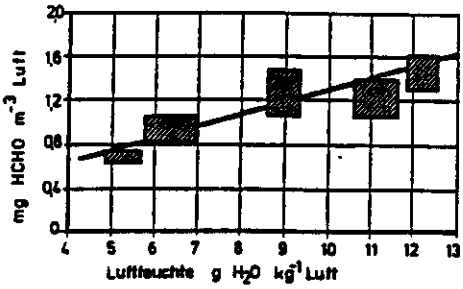

We can see the linear correlation between large chamber values and the humidity.

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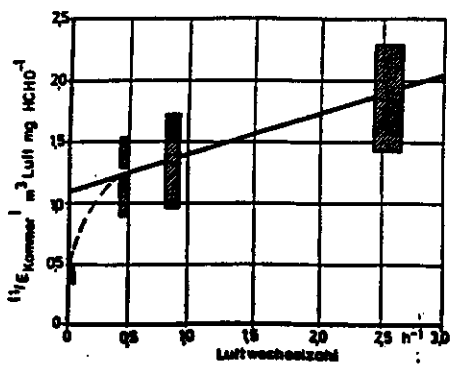


We can see the linear correlation between large chamber values and the charge (m^2 of board surface / m^3 of chamber) .

We will now describe the small scale lab methods .

The perforator method

The most common test on formaldehyde is the perforator test . We can see a scheme of this apparatus and also shortly describe the way it works .(slide). The board is cut in small pieces (2.5*2.5 cm) and approximately 100g of these are placed in a vessel which contains approx. 600 ml of toluene and is connected to the perforator . We heat the system to the boiling point. The formaldehyde is extracted from the wood by the toluene and then the toluene passes through water which extracts the formaldehyde before the toluene goes back to the vessel. After two hours of perforation the formaldehyde content in the water is determined. This is the perforator value. This method gives accurate results downwards to 7 mg of formaldehyde/100g of wood . Below this value the results are not very accurate. The perforator value depends much on the moisture content of the board. There is a correction equation, but this is not accurate when the difference from the standard 6.5% is big,especially at higher moisture contents and low molar ratio resins where we have a large amount of hydrolysis due to the elevated temperature of the extraction and the weakness of such resins. This method however is generally accepted for the classification of boards and is widely used. As mentioned before this method is the only method where mean of extraction is a liquid and belongs to the dynamic methods which determine the total amount of formaldehyde contained in the board.

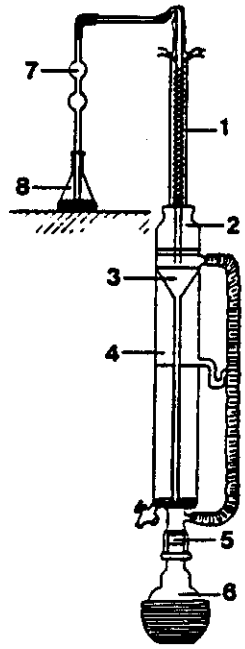
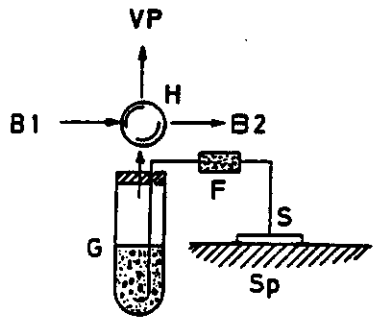


Abbildung 3.1 FESYP-Apparatur zur Bestimmung der Formaldehydabgabe von Spanplatten (Perforator).

The dynamic gas analysis methods

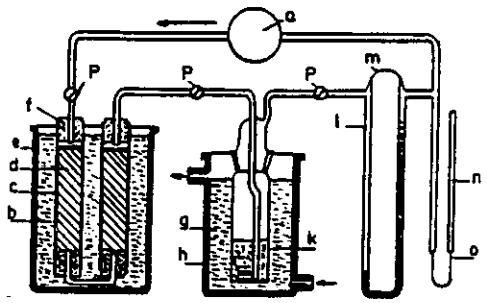
The sucking and splitting method

This method is easy, fast and does not destroy the board. (slide). We place a bell on the board and with a vacuum pump we suck a standard volume of air through the board and extract the formaldehyde that goes with it, with water. Then the formaldehyde contained in the water is measured. This method cannot be used for laminated boards. In this case we use the split method where, we cause a split in the board of standard dimensions and use the same procedure. This method is affected by the same parameters as the large chamber method, e.g. temperature, air-humidity etc.



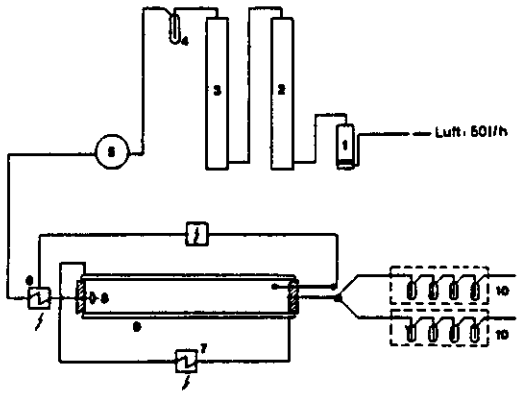
The gas analysis-method of Stoeger

In this method we start by grinding the sample. Then we place it in a cylinder and the cylinder in a thermostatic bath. Then we circulate air through the system. The air takes the formaldehyde and is then extracted with water. The formaldehyde content of the water is then determined. This method is not interesting for quality control.



The gas analysis-method of FESYP

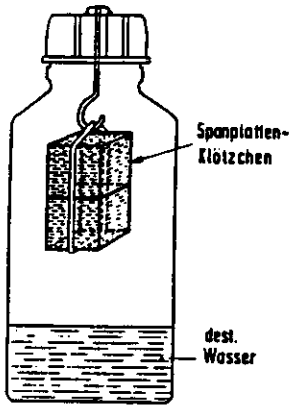
The principle of this method is the following : An air stream of 60 l/h is heated at 60°C and passed through a chamber that contains the sample with dimensions 400 by 50 mm . Then the formaldehyde is washed out with water. The formaldehyde in the water is determined and the value is called the gasanalysisvalue and has the dimensions mg/m^2h. For the calculation of this value we use the average values of the second, third and fourth hour of the test. The values during the first hour are not stable and therefore useless. The Frauenhoffer Institute for Wood research has developed an apparatus based on this method. The advantage of this method is that we have a large chamber simulation where we can test even coated boards. However, the ratio of edge to surface is very high.



The stationary gas analysis methods :

The WKI bottle-method

From the board we cut pieces 25 by 25 mm. We bind each time 15 g of these together and place them in 500 ml bottles, which contain 50 ml of water, so that they hang above the surface of the water. Then the bottles are placed in an oven at 40° C, each one for different periods of time. After the above mentioned procedure the bottles are placed in the refrigerator at -20°C for the formaldehyde to be absorbed by the water . Then the formaldehyde content of the water is determined either photometrically or jodometrically . The values become higher with the time, as it is obvious from the diagram. This method allows the detection of even small differences between boards which could never be detected with the perforator method. The differences between boards increase with the duration of the test. We have a good linear correlation between the 24 or 48 h WKI test and the perforator values of the samples as it is obvious from the diagrams but this is valid only downwards to 10 mg. The 24h WKI value of a board tends to be lower and the 48h value higher than the perforator value. The WKI-bottle method is generally accepted as a classification method but only if the correlation with the perforator test is precisely known. This method is one of the most widely used methods because its cheap and easy and the results do not depend on the moisture of the boards.



The modified Roffael method

The WKI method was modified and standardised in Netherlands. This modified method has as follows: A sample with dimensions 40 by 50 mm by thickness is placed in a bottle of standardised dimensions. This bottle contains 50 ml of a saturated NaCl solution. The relative humidity in the air above this solution at 40°C is 75%. The saturated NaCl solution is changed at fixed timeintervalls and the formaldehyde content in the NaCl solution is determined jodometrically. Between the modified Roffael method and the WKI method a simple linear relation exists. With this method, it is possible to test all kinds of boards and the results are almost independent of the boardmoisture. The ratio of edge to total surface, however, is still very high.

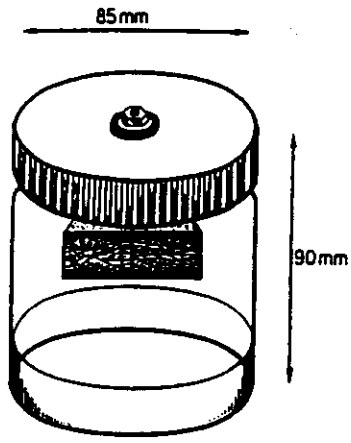
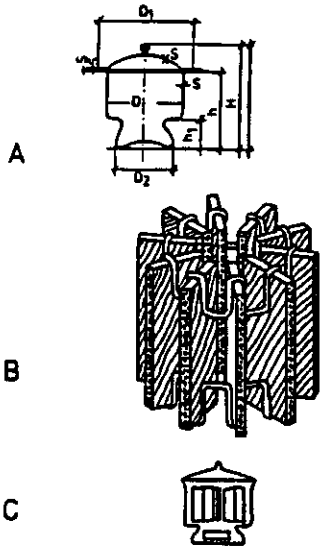


Abbildung 3.8 Modifizierte Roffael-Methode

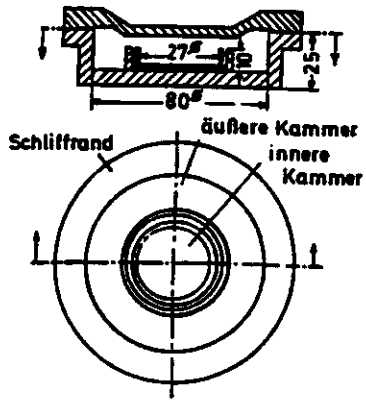
The dessiccator method

In this method we put 7-10 samples (50 by 50 mm) in a dessiccator which has standard dimensions and contains 300 ml of water. The dessiccator is kept for 24 h at 20-25 °C. Then the formaldehyde in the water is determined photometrically. This is the Japanese industry's standard method. The disadvantage of this method is still the very high edge to surface ratio. In the USA we saw recently a modification of this method in which again 7-10 samples of particleboard with dimensions approx. 70 by 150 mm are used for the test , but the edges of the samples are first sealed with molten paraffin. Then they used the same procedure as described above. The formaldehyde in the water was determined photometrically. There is a linear correlation between the dessiccatorvalue from the one side and the perforator and large scale chamber test from the other.



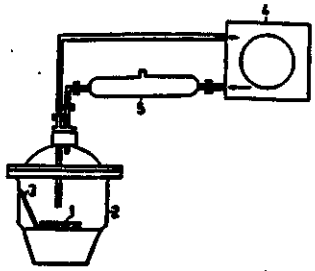
The micro diffusion-method

This method uses a very small container which is divided in two small chambers not separated from each other. One outer and one inner. From the outer chamber gas comes into the system and this gas is adsorbed from a solution in the inner chamber. We place a accurately weighted sample of grinded particleboard of approximately 1g in the outer chamber and the formaldehyde is adsorbed by a chromotropic acid solution in the inner. The main disadvantage of this method is that the sample has to be grinded fist and therefore we can no see the effect of laminating,coating etc. on the formaldehyde emissions.



The SINTEF method

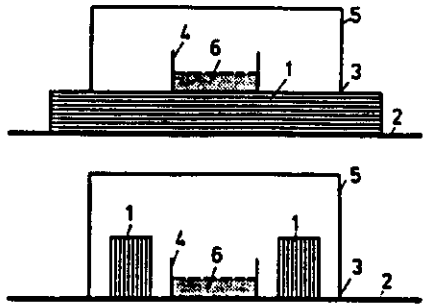
In this method we place a board sample of 100 by 100 mm in a dessiccator. The dessicator is connected to a membrane pump which circulates the air in the system. We do not inject fresh air. A siphon



mountedin this air circuit. After two hours of circulation the siphon is removed and the formaldehyde in the air is measured photometrically.

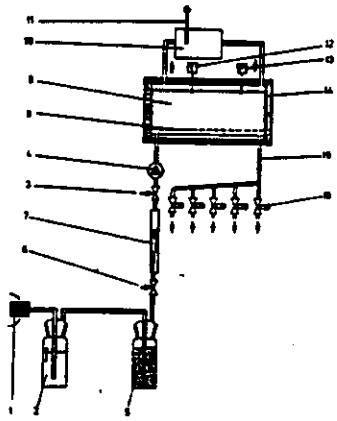
The FAHRNI method

In this method we use a large piece of particleboard. On this piece we put a small vessel with a solution of acetyl acetone in water. Then the sample is covered with an airproof vessel of standard dimensions . The whole thing is kept for 4 h at 20-22°C. The formaldehyde is adsorbed by the solution and is measured photometrically. This method detects only the formaldehyde which is released through the surface of the sample and is comparable to the chamber test with air exchange ratio of 0.



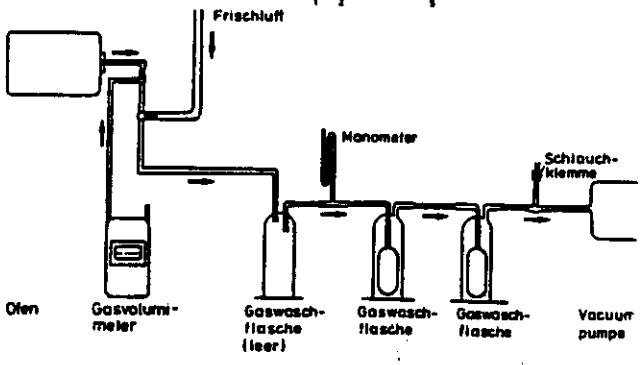
The gas analysis chamber of Wittmann

For this test we place two pieces of board of 530 by 440 mm in a climate chamber for two h at 70°C and 50% relative air humidity. 60 l of the formaldehyde containing air, are passed through a formaldehyde absorbing solution and the formaldehyde is measured jodometrically.



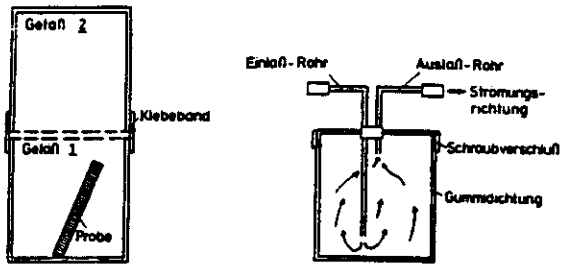
The TNO gas analysis method

A sample of 170 by 170 mm is placed for one week in a climate chamber at 20°C and 50% relative air humidity.Then the sample is placed in an oven at 60 °C and stored for one hour. The oven is gastight sealed. Then the oven is evacuated at 13.3 kPa and the air which contains the formaldehyde is passed through two bottles which contain a sodiumhydrogensulfite solution. The formaldehyde is measured with chromotropic acid.



The jar-method

The method consists in putting a board sample of 125 by 630 mm in a chamber similar to two aquariums placed one on top of the other and sealed gastight. After 24 h the upper piece of the chamber is removed and the formaldehyde containing air is blown out with an airstream and into a formaldehyde absorbing solution. In this solution it is then measured photometrically.



The large chamber test is the generally accepted method for the classification of boards. The results of this test depend, a lot as mentioned above, on external parameters, like temperature, air-humidity, air exchange ratio and charge-factor as well as on internal parameters like the quality of the board surface and the formaldehyde content of the board itself. By keeping all the external factors constant we will see that we have many combinations of surfaces and formaldehyde contents in boards which would give the same

large chamber value. For example a laminated board which is prepared with a high molar ratio resin (high formaldehyde content in the board) could give the same large chamber value like a non coated board produced with a low molar ratio resin. In order to understand the next method , the DMC method, we must firstly discuss the effect of the board surface on the large chamber value.

As mentioned before in the large chamber test the formaldehyde has to be released in the air in order to be measured. Since the ratio of edge to the total surface is very low, we can suppose that all this formaldehyde has to be released through the surface. This means that the structure of the surface is very important for the results. We describe the surface with its masstransfercoefficient or permeability. The following method allows an estimation of the permeability of the board surface and therefore a better understanding of the values obtained.

The DMC method.

This method, recently developed in the USA, consists of two different measurements. The measurement of the steady formaldehyde concentration, **Cs,** in a constant air stream and the measurement of the maximum formaldehyde concentration,Ceq, in the air surrounding the sample when the air stream is turned off. The permeability K of the board surface can be calculated with the following equation:

$$K = \frac{N \times C_s}{L \times (C_{eq} - C_s)}$$

The Cs value shows a linear correlation to the large chamber value of the board. The calculation of the permeability of the board provides us with more information about the manufacturing process.

For the test we place the samples (200 by 300 mm approximately) in the DMC chamber (after we seal the edges) and we measure Cs and Ceq. These values are measured by an electronic sensor. Of course these values are affected by the same parameters as in the large chamber. The software provided with the DMC, however, is supposed to give comparable results for all the cases.