



Formaldehyde analysis: Test methods and results

Dr. Song Ma, Dr. Matt Walker, Mark Bartle, Clariant Production UK Ltd

There have been recent changes in the understanding of the toxicity of formaldehyde, and a proposed change in the testing method. With the realisation that the greatest risk to human health comes from airborne formaldehyde, test methods are now tending to change to reflect this.

For some applications, for example automotive upholstery, where the test should reflect the potential release of formaldehyde into air it is necessary to re-evaluate formaldehyde testing methods and the errors that are associated with them.

Recent developments in scientific understanding and legal requirements

The International Agency for Research on Cancer (IARC), an executive agency for World Health Organization (WHO), reviewed the data of various studies on the toxicity of formaldehyde in 2004^[1] and concluded that “formaldehyde is carcinogenic to humans”.

For each project, experts from around the world were invited to review the available data from different research works. Based on the facts and following a set of clearly defined criteria, they drew their conclusions, which are highly respected and the leather industry, as with other industries, will have to further tighten controls on formaldehyde.

After years of research, surveying and monitoring information related to the ‘sick house syndrome’, the Japanese Building Standard Law (BSL) has been amended.

The amended BSL has ‘sick house’ regulations, which regulate

the volatile chemical products which are emitted from building materials.

JAMA (Japanese Automobile Manufacturers Association) took the view that the cabins of motor vehicles should be defined as ‘residential space’. Based on their own studies, JAMA announced in 2005 that it will pursue a voluntary approach to reduce the concentration of volatile organic compounds (VOC) in the cabins of passenger cars.^[2] It also recommended a test method based on the analysis of in-cabin air quality, and the restricted substances and their respective concentration guideline values (taken from reference 2) are listed as Panel 1.

It is clear that the restrictions on formaldehyde content, as well as other VOCs, will become even more stringent in leather processing chemicals and, of course, in the resultant leather.

In some cases, the requirement is nearly as low as the ambient background level. Therefore, it is necessary to review formaldehyde testing methods and also to analyse the potential sources of testing errors.

Test methods and their comparisons

There are four general methods used to test for formaldehyde:

TEST METHOD No. 1: TOTAL RECOVERY OF FORMALDEHYDE

In these types of methods, the products are broken down, with the aim of recovering all of the formaldehyde that was originally added during the manufacturing of the product. One of the typical methods is BS6806 part 1.

TEST METHOD No. 2: EXTRACTION OF FORMALDEHYDE FROM THE SUBSTRATE BY SOAKING IN WATER

Samples are soaked in water with or without surfactant to extract the water soluble products—including formaldehyde—from the substrate. This method has been widely used to test shoe uppers, leather goods and leather for toys. The main problem with such a method is that the leached extract can contain a significant quantity of chemicals that are based on formaldehyde such as syntan.

These formaldehyde containing chemicals may be broken down under testing conditions to form formaldehyde. Therefore the results from such a test are called ‘free and hydrolysable formaldehyde content’. Due to the nature of this test, the final results from this method can vary widely, depending on the specific testing conditions.

The typical methods using this route include: Japan law 112, JIS1041, BS6806 part 2, IUC19, ISO/TS17226:2003.

One particular point which is very worthwhile noting for this method is that the resultant extract liquor can be tested using two methods:

Colorimetric method: Under buffered conditions (*pH near neutral*), acetyl-acetone is reacted with formaldehyde, forming a yellow colour which is then measured on an UV-VIS spectrometer. ►

Panel 1:

Japanese new car interior air quality VOC limits

Formaldehyde	100 microg/m ³ (0.08 ppm)
Toluene	260 microg/m ³ (0.07 ppm)
Xylene	870 microg/m ³ (0.20 ppm)
Paradichlorobenzene	240 microg/m ³ (0.04 ppm)
Ethyl benzene	3800 microg/m ³ (0.88 ppm)
Styrene	220 microg/m ³ (0.05 ppm)
Cholorpyrifos	1 microg/m ³ (0.07 ppb)
Di-n-butyl phthalate	220 microg/m ³ (0.02 ppm)
Tetradecane	330 microg/m ³ (0.04 ppm)
Di-2-ethylhexyl phthalate	120 microg/m ³ (7.6 ppb)
Diazinon	0.29 microg/m ³ (0.02 ppb)
Acetaldehyde	48 microg/m³ (0.03 ppm)
Fenobucarb	33 microg/m ³ (3.8 ppb)



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HPLC method: DNPH (*dinitrophenylhydrazine*) can react with aldehydes (*including formaldehyde and ketones*) to form a compound which can be measured using UV-VIS spectrometry. Through HPLC separation, this method can quantitatively measure the content of aldehydes and ketones. The reaction can be carried out in organic media (*solvent*) or with phosphoric acid for example.

Obviously the pH levels will be very different between the colorimetric and HPLC methods, which will lead to variations in the apparent free formaldehyde content returned by the analysis.

TEST METHOD No. 3: EXTRACTION OF FORMALDEHYDE USING SATURATED WATER VAPOUR (SEALED JAR)

For this method, test specimens are suspended in sealed jars (*with support if necessary*) which contain a little distilled water. At an elevated temperature, the saturated water vapour will extract the volatile chemicals from the substrate. The aqueous solution can then be tested for formaldehyde by either colorimetric or HPLC evaluation as above.

This test method has been favoured by textile and automotive producers and their customers. Typical methods include JIS1041, AATCC-112, BS6806 part 3, ISO14184-2 and some specifications from individual companies such as Volkswagen.

This method has the obvious advantage that only relevant volatile components can be extracted and interference from the substrate will be minimal. However, the test conditions are very harsh and some chemicals can dissociate under such conditions to give higher apparent results (*'false positives'*) as already highlighted.

TEST METHOD No. 4: EXTRACTION OF FORMALDEHYDE USING GASEOUS MEDIA

This method has become the recent trend for several applications such as:

- Determining the levels of free formaldehyde of certain commercial goods in transit
- For internal building or vehicle air quality checks

In this method, the substrates (*which could be leather or leather processing chemicals*) are leached using nitrogen or air at an elevated temperature. Typical test methods are the draft method IUC 26 for leather auxiliaries, the recently adopted JAMA vehicle chamber testing, and some specifications from individual companies such as Toyota.

Significance of the various test methods

All test methods above are successful in recovering formaldehyde intentionally added to inert substrates (*'spiked' substrates*), with recovery rates of between 85-105%. However, the values obtained for so-called 'free' formaldehyde derived from hydrolysable formaldehyde compounds in the substrate are very dependent on the method used. Large variations are found for so-called 'free' formaldehyde between one method and another. This is illustrated in *Panel 2*.

A similar or even greater variation of 'free' formaldehyde content with test methods is shown when analysing products, as illustrated in *Panel 3* in the case of an amino resin syntan.

It is of course known that such resins are susceptible to hydrolysis, especially under acid conditions. Accordingly, it is clear that both test methods involving the use of water have hydrolysed the test specimen to give an artificially high reading.

Panel 2:

Formaldehyde contents of some commercially produced leathers when tested by different methods

Leather samples	Water extraction 40°C 1 hour plus surfactant	Vapour extraction 60°C 3 hours	Vapour extraction 49°C 20 hours
1	3.7 ppm	8.5 ppm	8.6 ppm
2	37 ppm	36 ppm	131 ppm
3	90 ppm	61 ppm	174 ppm
4	204 ppm	265 ppm	660 ppm
5	387 ppm	379 ppm	1100 ppm
6	143 ppm	71 ppm	409 ppm
7	302 ppm	160 ppm	475 ppm

Results are expressed as parts per million (ppm) on the weight of the leather as received.

Panel 3:

Formaldehyde content of an amino resin syntan

Test method	Formaldehyde content (ppm)
Water soaking method (procedure 2)	35000
Vapour extraction method (procedure 3)	12000
Gaseous extraction method (procedure 4)	450

Results are expressed as parts per million (ppm) on product as received for analysis.

This variation in the apparent 'free' formaldehyde with general test types makes it essential to select the method most appropriate for the particular application concerned. For example, the formaldehyde-related hazards of handling/transporting products are arguably best assessed via a method of the headspace type (*Method No. 4*). Effects on leather during processing, on the other hand, might be better reflected using a solution (*Method No. 2*).

Many other factors can also affect the formaldehyde test results in leather. One particular area of concern is the lack of inter-laboratory correlation of test results (*see Annex A, Draft IUC 19, JSLTC, 82(6), 1998*). Although widely acknowledged, it is very difficult to quantify the differences. As all of the results for this work are from the same Clariant laboratory, it is not necessary to discuss this aspect further here.

Another potential factor influencing the testing of leather is the locational effect on the hide or skin, for example, samples from different locations on the same hide will give different results.

The origin of formaldehyde and its implications

The most important factor has to be the reactivity/stability of the relevant compounds within the leather. From a chemical point of view, formaldehyde-based products can reverse their formation process under certain conditions, releasing formaldehyde as they do so.

With reference to Test Method No. 2: The water soluble compounds will be extracted from the testing substrate into the extraction medium (*water*). During the testing process, ➤



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these compounds will come into contact with the reagent molecules. From the chemistry of the formaldehyde reaction, it is believed that formaldehyde could form a compound with a wide range of chemicals and most formation reactions are equilibrium reactions, i.e. the reaction will only reach a certain balance. Obviously, the point of equilibrium will shift, depending upon the conditions. When the temperature, pH and pressure are fixed, the shift of the reaction will be driven by the concentration. When in contact with an appropriate reaction partner (*usually very active and highly reactive with formaldehyde*), free formaldehyde will be quickly consumed and the equilibrium will shift towards dissociation. More and more formaldehyde will thus be produced and reacted.

Although it had previously been extrapolated based on the chemistry of these compounds, Clariant was the first to actually publish test results to support the hypothesis^[3]. In that work, a 'model formaldehyde containing compound' at different concentrations was reacted with a formaldehyde derivative agent and then the apparent formaldehyde content was assessed. The results show that with a decrease in the concentration of the formaldehyde containing compound, the apparent formaldehyde content increases sharply, as shown in *Panel 4*.

With reference to *Panel 4*, the so-called 'Series 1' shows the actual experimental results and the solid black line is the best-fit by computer. It is clear that, as predicted by equilibrium theory, the apparent formaldehyde content of a given substance will increase sharply with the decrease of concentration of that substance in the test solution. This result demonstrates the importance of concentration. A relatively innocuous material could produce a very high apparent formaldehyde content when tested at low concentration.

With reference to Test Method 3: The test samples are extracted by saturated water vapour at an elevated temperature for a prolonged length of time. Although the conditions appear to be lenient, they are actually very harsh for formaldehyde-containing chemicals. The intermediate product of formaldehyde reaction is methylol group. The methylol group is chemically attached to the compound and it is usually stable, however, under the conditions of saturated water vapour, some of the methylol groups will be converted into formaldehyde. The data in *Panel 2* shows that the longer the extraction time, the higher the conversion rate to formaldehyde. Therefore this procedure will recover both free

formaldehyde and the formaldehyde formed during the extraction process. In other words, the final result will be decided, to a large degree, by the saturated water vapour stability of the formaldehyde-containing compound.

It is therefore obvious that both test methods 2 and 3 could produce rather misleading results.

The formaldehyde containing compounds, polymers or not, are generally stable and have no detrimental properties related to formaldehyde. During the test procedures, however, these compounds could be broken down to produce free formaldehyde. Therefore, the applicability of these procedures needs to be carefully considered.

The recent trend on formaldehyde testing and work to satisfy the requirements

In the past, formaldehyde test method selection for leather was mainly based on two criteria:

- If the target leather is likely to come into direct contact with human skin (*e.g. shoe uppers, watch straps*), the water extraction method is used.
- If it is more likely that the substances that are released from the leather will be inhaled (*e.g. automotive upholstery*), the vapour extraction method is used.

Recent scientific evidence has indicated that the major health concerns about formaldehyde are the effects on the upper respiratory tract. Therefore, the most important control should be placed on the level of formaldehyde which is emitted into breathable air space. It appears that this fact has been recognised by various organisations.

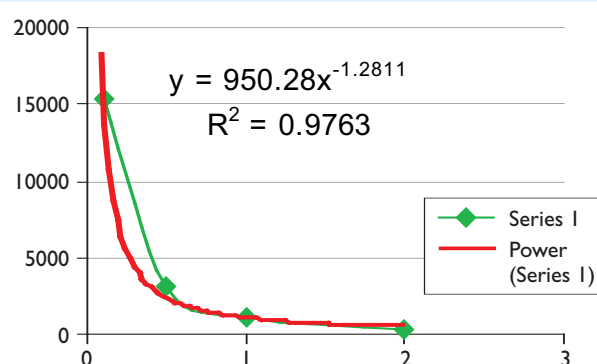
The following two examples highlight the trend of current requirements:

- Draft IUC 26^[4] is a gas extraction-based formaldehyde testing method. With this method, products are extracted with high purity nitrogen at an elevated temperature to make sure that all of the volatile formaldehyde is extracted. The nitrogen gas passes through a trap (*cartridge containing silica coated with DNPH*). The formaldehyde in the gas is trapped by the DNPH and the content of the cartridge is discharged and then tested by HPLC/UV detection. It is anticipated that this method will be used in assessing free formaldehyde content in leather auxiliaries, especially for transport and handling purposes.
- In a separate development, formaldehyde analysis has also been integrated into general VOC testing leather for interior uses such as auto upholstery. VOC testing is obviously not new, but the requirement for tanners to supply leather which meets volatile formaldehyde requirements is a relatively recent development. With this type of test an integrated approach is taken. The important factor is not the performance of a single item but the sum of the whole system, for example, the whole house or the whole car. Currently tanners are only facing requests for this from Japanese automobile manufacturers following the decision by JAMA. In this type of assessment, the air quality in the passenger cabin is measured. It is not clear whether other countries will follow this lead.

One fact worth noting is that acetaldehyde also appears on certain lists of restricted substances (*see Panel 1*).

Panel 4:

The apparent formaldehyde content vs. concentration of formaldehyde containing compound - Schematic representation





How to satisfy current legal and commercial requirements

There are two basic ways to meet the challenge of low free formaldehyde leather:

Avoidance: Using aldehyde free chemistry to develop new products.^[Legend]

Treatment: Aldehyde-based products can be treated in several ways in order to reduce the free and releasable formaldehyde levels. When different methods are employed, leather processing products with exceptionally low levels of free formaldehyde can be produced.^[Legend]

Accordingly, new formaldehyde free and low formaldehyde products have been developed to support the production of low free formaldehyde leathers, to meet current demands in the market.

Summary

In this work, we have highlighted the recent developments in formaldehyde testing in leather. The general situation is that the requirements have become clearer, however, the required levels of formaldehyde are becoming increasingly lower, not necessarily just in the leather, but also in the processing of products and the environment. 

References

1. IARC news release, <http://monographs.iarc.fr/ENG/press-release/archives/pr153a.htm>
2. JAMA announcement; <http://www.jama-english.jp/release/2005/050214.htm>
3. S. Ma; *Proceedings of the 7th Asian International Conference of Leather Science and Technology*, Section 1, p16, 15th October 2006, Chengdu, China
4. Draft IUC 26, *Leather – Chemical tests – Determination of free formaldehyde in process auxiliaries*

Legend

Aldehyde free products by Clariant:

- Tergotan PMB Liquid: Polymer retanning agent
- Tergotan TSP Liquid: Polymer retanning agent

Reduced formaldehyde products (RF Range):

- Tanicor CRF Powder: A phenol based retanning agent for automotive and soft leather types
- Tanicor DRF Powder: A phenol based retanning agent for shoe upper, especially white
- Cartan ERF Powder: Naphthalene dispersing agent with capacity to absorb free formaldehyde from the leather
- Tergotan ARF Powder: Melamine based resin for all leather types



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