Determination of Formaldehyde Content in Leather: EN ISO 17226 Standard. Influence of the Agitation Method Used in the Initial Phase of Formaldehyde Extraction

by
Albert M Manich,[1]* Sara Cuadros,[1] Joaquim Font,[2] Anna Bacardit,[2] Felip Combalia[2] and Agustí Marsal[1]
[1] *Instituto de Química Avanzada de Cataluña, IQAC-CSIC,*
C/ Jordi Girona, 18-26, Barcelona, Spain
[2]*Cátedra A3, Escola d'Enginyeria Igualada,*
Avda Pla de la Massa 8, Igualada, Spain

Abstract

Given the carcinogenic character of formaldehyde, it should be reliably determined in any substrate. The EN ISO 17226 Standard is the Official Method to quantify formaldehyde in leather. However, some misunderstandings may arise from the practical conditions given by the Standard for the extraction of formaldehyde. Two agitation methods (magnetic agitation and reciprocal linear agitation), which fulfill the conditions of the Standard, have been used for the extraction of formaldehyde in twenty two samples of wet-blue split leather treated with resins synthesized with formaldehyde and with/without the addition of vegetable compounds. The agitation method influences the formaldehyde content and differences between the agitation methods depend on the formaldehyde resins and vegetable compounds applied. Magnetic agitation leads to formaldehyde contents that are 26% greater than those obtained when the reciprocal linear agitation method is used. Major brands specify allowable limits for formaldehyde content, which depend on the user (adult or babies) and whether the article is in direct contact with the skin. A high percentage of disagreement (33.3%) has been observed between the agitation methods in fulfilling the allowable limits. One-third of the formaldehyde content results that fulfilled the allowable limits with the reciprocal linear agitation method failed when the magnetic method was applied. The situation urges the clarification of the shaking method in the EN ISO 17226 Standard to avoid the high level of contradictory results between methods that meet the agitation conditions of the Standard.

Introduction

Formaldehyde, which is the simplest aldehyde (methanol), is a colorless and pungent gas at room temperature. Being water soluble, formaldehyde is commercially available in aqueous solutions with a formaldehyde content that varies from 37 to 50%, known as formalin. At concentrations above 0.1 mg/kg in air, formaldehyde can irritate eyes and mucous membranes although its odor threshold is higher (about 1 ppm).

The Washington State Department of Labor and Industries studied in 2001 the possibility of dermatitis due to the contact of the user with the leather article. It has been reported that, in contact with skin, formaldehyde derivatives cause allergic contact dermatitis when used in textiles.[1] Recently, a carcinogenic character to humans has been attributed to formaldehyde.[2-3]

Formaldehyde has application in many sectors. In the chemical industry it is used as an intermediate in the production of resins and other industrial chemicals, as a preservative in some paints and, because of its bactericidal properties, as a component in the formulation of cosmetics.

However, it is in the tanning industry, specifically in the retanning operation, where formaldehyde has a wide application either as syntan (condensation products of phenols and naphtols with formaldehyde) or as resin (condensation products of amines, amino acids, etc. with formaldehyde).[4] These formaldehyde resins, due to certain conditions, are susceptible to partial hydrolysis and release formaldehyde.[5] But, not only formaldehyde from resin hydrolysis is detected in leather but also that coming from an excess in resin preparation or that used in some operations in leather manufacture. It should be pointed out that in a study carried out in 2008, double face leathers with high formaldehyde content were found.[6]

*Corresponding author e-mail: albert.manich@iqac.csic.es
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Because the carcinogenic character attributed to formaldehyde[2-3] and other restrictions that some countries have on its presence in consumer articles, recent market studies and research papers suggest the production of leather articles free from formaldehyde[7-9] or that its presence is below allowable limits. Major brands include limits for formaldehyde content in their "restricted substances list", limits that depend on the user (adult or babies) and whether the article is in direct contact with the skin (Table I). The majority of brands set allowable limit below 20 mg/kg for children, while the Afirm Group set the limit at 50 mg/kg for children and adults. If goods are in direct contact with skin, the allowable limit is 75 mg/kg although Levi Strauss set the limit at 65 mg/kg.

Of the analyses carried out on the formaldehyde content in leather for footwear from Asia in the "A3 Chair in Leather Innovation" of the Universitat Politécnica de Catalunya since 2013, the 16% of the samples gave rise to a formaldehyde content higher than 75 mg/kg, i.e., the 16% of leathers failed the requirements of four or five major brands. This percentage of fails is even higher for the particular case of double face skins, in which nearly 30% of all the analyzed samples had formaldehyde content higher than 75 mg/kg.[10]

Table I
Allowable limits for formaldehyde content in the "restricted substances lists" of major brands.

BRAND	CURRENT LIMIT (mg FM/kg)		
	Adults / General	Children / Babies	Direct contact with skin
Inditex	300	20	75
H&M	300	Absorbance differences: 0.05	75
Nike	---	20	75
VFC (Kipling, Vans Off The Wall, Eastpack i The North Face)	300	20	75
Afirm Group (Carhartt, SPIRIT, GAP, Puma, New Balance)	Textile: 20 Leather: 50	Textile: 13 Leather: 50	
Mango, G-Star	Standard OEKO-TEX ®		
Levis Strauss	250	16	65

Therefore, it is of paramount importance to have an analytical method to reliably determine the formaldehyde content in any substrate. In the case of leather, the EN ISO 17226 Standard is the Official Method with this objective. This Standard consists of three parts. In the first part, the quantification of the formaldehyde extracted from leather is carried out by reverse phase HPLC[11] whereas, in the second, quantification is carried out by colorimetry at 412 nm.[12] In both methods, the initial phase of extraction of formaldehyde present in leather is common and it is carried out with a suitable surface active agent. In the third part of the Standard, the leather sample is not in direct contact with the extraction solution and the method determines the formaldehyde emitted by the sample.[13]

In a previous work, a revision of the Official Standard EN ISO 17226 (Parts 1 and 2) "Determination of formaldehyde content in leather" was conducted because, in authors' opinion, certain operations of the methods could be improved and some phrases of the Standard were ambiguous and could lead to misunderstandings.[14] The agitation method to be used for extracting the formaldehyde present in leather was one of the operations considered in that study. The authors considered that the sentence "***Stir*** the content of the flask *or* ***shake smoothly*** at 40°C ± 0.5°C in a water bath for 60 min ± 2 min", included in the text of the Standard, was somewhat ambiguous since the method of agitation could influence the results of formaldehyde extracted from leather. Two agitation methods that fulfill the conditions of the sentence (magnetic agitation and linear reciprocal agitation) were used in the initial phase of formaldehyde extraction from wet-blue split leather subjected to different treatments. The authors found that magnetic agitation gave higher results of formaldehyde content than lineal reciprocal agitation and that the difference between results obtained with both methods was significant.

Given that this initial study[14] was conducted with only six leathers subjected to different treatments, the authors felt appropriate to expand the study with a larger number of leathers so that the conclusions were more definite.

Objectives

The purpose of this study is to check if two agitation methods (magnetic agitation and reciprocal linear agitation), which fulfill the conditions of the sentence "***Stir*** the content of the flask *or* ***shake smoothly*** at 40°C ± 0.5°C in a water bath for 60 min ± 2 min", included in the text of the EN ISO 17226 (Parts 1 and 2) Standard, give similar results in the analysis of

formaldehyde present in leather samples. Contrarily, if both agitation methods provide different results of formaldehyde content in the analyses of the same leathers, the above mentioned sentence must be revised and the Official EN ISO 17226 Standard must specify more clearly the type of agitation to be used in the extraction phase of formaldehyde from leather.

Twenty two samples of wet-blue split leather treated with formaldehyde resins and with/without the addition of vegetable compounds were analyzed for their formaldehyde content in accordance with the EN ISO 17226-2 Standard in which the quantification of formaldehyde is carried out by colourimetry.[12] Magnetic agitation and reciprocal linear agitation were used in the initial phase of extraction of formaldehyde from leathers. Table II shows the different retanning treatments to which the analyzed leathers were subjected. Given that in a previous work it was found that the formaldehyde content in leather samples varied as a function of the time elapsed after production treatments,[14] formaldehyde content was determined at 30, 60 and 90 days after treatments.

Materials

Butts of wet-blue splits shaved to a thickness of 1.5 mm of German cowhides supplied by Despell S.A were the starting material. Working only with this type of substrate minimizes the influence of hide area on the absorption of chemicals and facilitates their penetration. Once received from tannery, the splits were subjected to the following conventional recipe in which percentages into brackets are offers on shaved wet-blue weight. After a wetting operation, a rechroming process was performed with chrome sulphate of 33% basicity (4%) and sodium-aluminium silicate (1%). Afterwards, neutralization followed with sodium formate (2%) and sodium bicarbonate (1%) before the retanning operation, which was different in each of the twenty two assays conducted. In all the treatments, the retanning process was carried out with acrylic resin (3%) and formaldehyde-based resins (5%). Depending on the assay, melamine-formaldehyde (MF) resin or dicyandiamide-formaldehyde (DCDF) resin at two levels of formaldehyde content (A: low; B: high) were employed. In addition to formaldehyde-based resins, the retanning operation was carried out with/without the addition of vegetable compounds. In a previous work,[15] it was concluded that vegetable extracts, mainly mimosa, decreased the formaldehyde content in leathers treated with formaldehyde-based resins and that this diminution was accentuated with ageing. Vegetable compounds considered in this work were: mimosa extract (MIM) (Clarotan, supplied by Tanac), quebracho extract (QUEB) (Indusol ATO, supplied by Silva) and tara powder (TARA) (Ormotan T, supplied by Silva). All these vegetable compounds were applied at offers of 2% (on shaved wet-blue weight) along with the mimosa and quebracho at offers of 4%. After retanning, fatliquoring operation was performed with chemicals of common use in tannery (8% of synthetic sulphated oil and 4% of phosphoric ester based oil), supplied by Pulcra Chemicals S.L. Once dried, determination of formaldehyde content in the treated leathers at 30, 60 and 90 days after leather processing were carried out. The samples for analysis were maintained at the same conditions during this period: they were placed in sealed plastic bags, which were maintained in the dark at 23°C and 50% relative humidity.[16]

Table II shows the twenty two different retanning treatments studied in this work.

Methods

Determination of Formaldehyde in Leather

The formaldehyde content in the splits subjected to the treatments presented in Table II was determined in accordance with the EN ISO 17226 Standard "Determination of formaldehyde content in leather. Part 2: Quantification by colorimetric analysis"[12] at 30, 60 and 90 days after leather processing.

In accordance with the method of the Standard, formaldehyde is first extracted from leather with sodium dodecyl sulphonate. However, we used sodium dodecyl sulphate instead of sodium dodecyl sulphonate because a previous research has demonstrated that the results obtained using one or the other surfactant does not have significant differences between them.[14] High purity sodium dodecyl sulphate is cheaper and easier to obtain. For the extraction, two different agitation methods were used to check if they provide similar results of formaldehyde content in the analysis of the same leather samples: i) reciprocal linear shaker at 40 strikes per minute (Selecta, Unitronic OR) (Figure 1a) and ii) magnetic shaker (Selecta, Multimatic-5S shaker base and Termotronic resistance) (Figure 1b). Once extracted and after filtration, the formaldehyde present in the filtrate was colorimetrically determined by measuring the absorbance at 412 nm after reaction with acetylacetone solution in ammonium acetate and glacial acetic acid medium.

Figure 1a. Reciprocal linear shaker.

Figure 1b. Magnetic shaker.

Two samples from each treatment were analyzed and three replicates for each sample were performed. The experimental result of formaldehyde content for each treatment is the mean value of six measurements.

Analysis of Formaldehyde Content in Formaldehyde Resins

The formaldehyde content in the formaldehyde-based resins used was determined by an adaptation of the EN ISO 17226 Standard "Determination of formaldehyde content in leather. Part 1: Quantification by HPLC".[11] In summary, a given amount of formaldehyde-based resin was extracted with sodium dodecyl sulphate solution. Once extracted and after filtration, an aliquot of the filtrate was reacted with dinitrophenylhidrazine and, afterwards, the formaldehyde was determined by HPLC. Five replicates of the analysis of formaldehyde content in the resins were performed. The following results ± 95% confidence interval were obtained: MF (A): 4514±326 mg/kg; DCDF (A): 6428±466 mg/kg; MF (B): 23481±369 mg/kg and DCDF (B): 21216±1000 mg/kg.

Analysis of Tannins and Non-tannins in Vegetable Compounds

Tannin and non-tannin content determination was carried out in accordance with the EN ISO 14088 Standard "Quantitative analysis of tanning contents by filter method".[17] This method consists of the indirect gravimetric analysis of vegetable tanning agents by the fixing of the absorbent compounds on hide powder with low chromium content.

Five replicates of the analysis of tannins and non-tannins in the vegetable compounds were carried out. The following results ± 95% confidence interval were obtained: Mimosa extract (Tannins: 70.1±1.7; Non-tannins:19.8±1.1); Quebracho extract (Tannins: 72.3±1.6; Non-tannins:16.3±1.0) and Tara powder (Tannins: 49.9±1.8; Non-tannins:17.0±1.2).

Regression Analysis

Linear regression analysis was used to compare the formaldehyde content obtained using the magnetic shaker ($[FC]_{MS}$) with respect to that obtained with the reciprocal linear shaker ($[FC]_{RLS}$) for all sets of samples classified according to the formaldehyde-based resins employed and the vegetable compounds added. Linear regression analysis between agitation methods has been used because it can be expected that the higher the content of formaldehyde in the leather sample, the greater the formaldehyde extracted regardless the agitation method employed.

The different sets of samples used in the linear regression analysis are:

Samples treated with Melamine-formaldehyde of low formaldehyde content:	MF (A)
Samples treated with Dicyandiamide-formaldehyde of low formaldehyde content:	DCDF (A)
Samples treated with Melamine-formaldehyde of high formaldehyde content:	MF (B)
Samples treated with Dicyandiamide-formaldehyde of high formaldehyde content:	DCDF (A)
No vegetable compound added:	REF or REFERENCE
With Mimosa at 2% and 4%: MIM4, grouped as	MIM2 and MIMOSA
With Quebracho at 2% and 4%	QUEB2 and QUEB4, grouped as QUEBRACHO
With Tara at 2% and 4%	TARA2 and TARA4, grouped as TARA

Results and Discussion

Table II shows the formaldehyde content in splits treated with different formaldehyde resins and vegetable compounds in the analyses carried out at 30, 60 and 90 days after leather processing for the two different agitation methods (Reciprocal linear shaker, RLS, and Magnetic shaker, MS) used in the formaldehyde extraction phase.

Due to the ambiguity of the sentence "***Stir*** the content of the flask ***or shake smoothly*** at 40°C ± 0.5°C in a water bath for 60 min ± 2 min" in the formaldehyde extraction phase of the EN ISO 17226 (Parts 1 and 2) Standard, two different agitation methods (the reciprocal linear shaker RLS and the magnetic shaker MS) have been employed to study the possible effect of the agitation method on the formaldehyde extraction and, therefore, on the determination of the formaldehyde content in the treated leathers.

Table II

Formaldehyde content according to resin. vegetable extract treatment and days elapsed after the treatment.

RESIN	Vegetable extract TREATMENT	Formaldehyde content (mg/kg)					
		Reciprocal Linear Shaker			Magnetic Shaker		
		30 days	60 days	90 days	30 days	60 days	90 days
MF(A)	REF	51.47	57.59	62.95	65.43	70.47	75.30
	MIM2	52.00	43.67	43.58	65.10	64.40	59.20
	QUEB2	53.08	54.06	56.76	67.90	71.20	74.40
	TARA2	57.04	59.99	63.57	68.90	72.70	73.30
MF(A)	REF	47.72	51.89	56.33	65.35	68.55	69.45
	MIM4	34.23	26.55	19.37	44.10	39.40	30.50
	QUEB4	51.05	48.30	46.77	66.11	62.40	62.30
DCDF(A)	REF	39.22	42.69	44.06	46.59	50.40	52.30
	MIM2	19.97	16.40	15.02	24.09	21.90	21.20
	QUEB2	24.10	24.28	21.71	32.90	29.40	28.30
	TARA2	26.96	22.80	20.54	34.70	30.80	29.90
DCDF(A)	REF	39.81	43.23	44.35	46.50	49.10	52.30
	MIM4	11.02	8.47	7.45	14.30	12.70	11.80
	QUEB4	14.67	12.65	10.10	21.20	17.10	14.10
MF(B)	REF	213.40	220.20	227.10	273.00	308.20	305.60
	MIM4	138.80	114.60	101.00	155.00	140.00	126.40
	QUEB4	208.00	186.80	174.90	235.00	233.60	225.00
	TARA4	198.40	183.90	171.40	254.00	241.50	227.20
DCDF(B)	REF	146.90	156.70	161.90	178.30	182.60	186.60
	MIM4	54.80	53.40	52.42	71.20	66.80	64.60
	QUEB4	99.90	81.20	76.49	108.70	104.70	101.30
	TARA4	81.40	75.40	74.48	106.90	94.20	88.00

To this end, regression equations relating the formaldehyde content given by the two agitation methods have been determined. Different sets of samples classified according to the resins and/or vegetable compounds used have been compared to evaluate if they can affect the linear regression equations.

Regression equations of individual sets have been compared in pairs using the method described by R. Mead.[18] This method is based on the residual sum of squares (RSS) given by the analysis of variance of the regressions. The RSS of the individual sets is compared with the RSS of the combined set through the F test and the result enables us to determine the signification level of the differences between the regressions of the individual sets.

Influence of the Formaldehyde Content (low, A or high, B) of the Melamine-formaldehyde Resin on the Formaldehyde Content (FC) of the Treated Leather Samples Extracted with the Two Agitation Methods

The regression equations FC_{MS} vs. FC_{RLS} for leather samples treated with melamine-formaldehyde resin of low formaldehyde content, MF(A), high formaldehyde content, MF (B), and for the combined set, MF (A)&MF(B), are:

MF(A): $FC_{MS} = 13.45 + 1.02 \times FC_{RLS}$ r = 0.972

MF(B): $FC_{MS} = -24.02 + 1.41 \times FC_{RLS}$ r = 0.970

MF(A)&MF(B) $FC_{MS} = 0.34 + 1.28 \times FC_{RLS}$ r = 0.993

The signification level of the differences between MF (A) and MF (B) is obtained by applying the method described by R. Mead.[18]

Source of variation	RSS	df	s^2	$F_{2.29}$	Signification level
Combined MF(A)&MF(B)	2916.63	31			
Individual MF(A) + MF(B)	2420.24	29	83.46		
Combined – MF(A) – MF(B)	496.39	2	248.20	2.97	10%

Figure 2 shows the formaldehyde content in leather samples treated with melamine-formaldehyde resins of low and high formaldehyde content as a function of the agitation method used in the extraction phase.

As observed in Figure 2, the formaldehyde content in leathers treated with melamine-formaldehyde resin is higher when the magnetic shaker is used in the formaldehyde extraction phase instead of reciprocal linear shaker.

The relationship between the two agitation methods is slightly significant affected by the type of melamine-formaldehyde resin. Growing rates in formaldehyde content after magnetic agitation when compared with results after reciprocal linear agitation are 1.02 for MF (A) and 1.41 for MF (B).

Influence of the Formaldehyde Content (low, A or high, B) of the Dicyandiamide-formaldehyde Resin on the Formaldehyde Content (FC) of the Treated Leather Samples Extracted with the Two Agitation Methods

The regression equations FC_{MS} vs. FC_{RLS} for leather samples treated with dicyandiamide-formaldehyde resin of low formaldehyde content, DCDF(A), high formaldehyde content, DCDF (B), and for the combined set, DCDF(A)&DCDF(B), are:

DCDF(A): $FC_{MS} = 4.27 + 1.08 \times FC_{RLS}$ r = 0.995

DCDF(B): $FC_{MS} = 9.85 + 1.11 \times FC_{RLS}$ r = 0.992

DCDF(A)&DCDF(B): $FC_{MS} = 3.18 + 1.16 \times FC_{RLS}$ r = 0.997

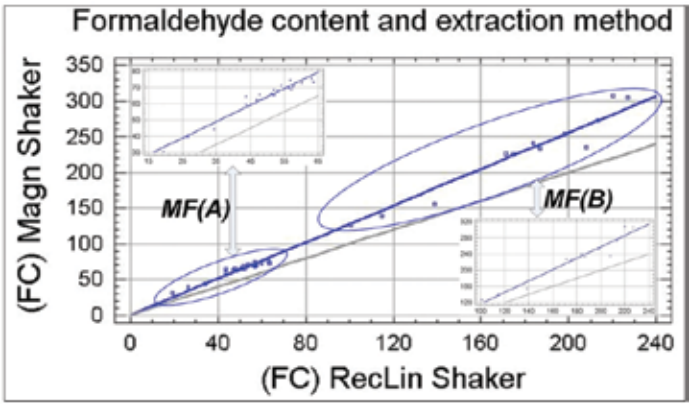

Figure 2. Linear regression relating formaldehyde contents obtained after extraction with magnetic shaker and reciprocal linear shaker of leather samples treated with MF (A) and MF (B) resins.

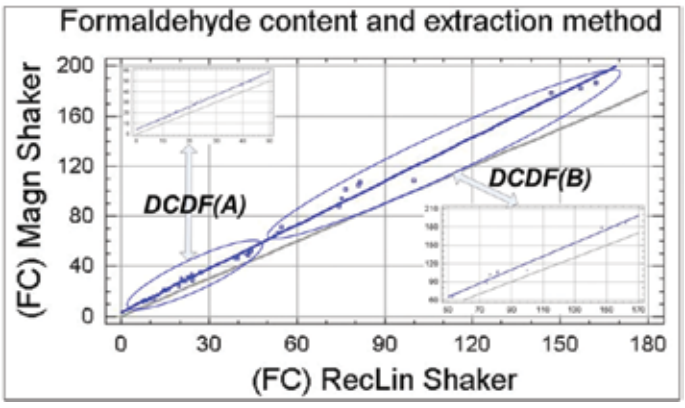

Figure 3. Linear regression relating formaldehyde contents obtained after extraction with magnetic shaker and reciprocal linear shaker of leather samples treated with DCDF (A) and DCDF (B) resins.

By applying the method described by R. Mead[18], it is possible to determine the signification level of the differences between DCDF (A) and DCDF (B):

Source of variation	RSS	df	s^2	$F_{2.29}$	Signification level
Combined DCDF(A) & DCDF(B)	491.19	31			
Individual DCDF(A) + DCDF(B)	372.61	29	12.85		
Combined – DCDF(A) – DCDF(B)	118.58	2	59.29	4.61	5%

Figure 3 shows the formaldehyde content in leather samples treated with dicyandiamide-formaldehyde resins of low and high formaldehyde content as a function of the agitation method used in the extraction phase.

Although the formaldehyde contents of splits treated with dicyandiamide-formaldehyde resin are lower than those treated with melamine-formaldehyde resin, the correlation coefficients are higher than 0.99, which means the existence of a linear relationship between FC_{MS} and FC_{RLS}, that is stronger than that observed for melamine-formaldehyde resin. The regression between methods depends on the formaldehyde amount of the samples treated with DCDF resins of different formaldehyde content. As occurs with MF resins, the magnetic shaker provides higher formaldehyde content than the reciprocal linear shaking. The greater the formaldehyde content (DCDF (B)) resin, the higher the differences between agitation methods.

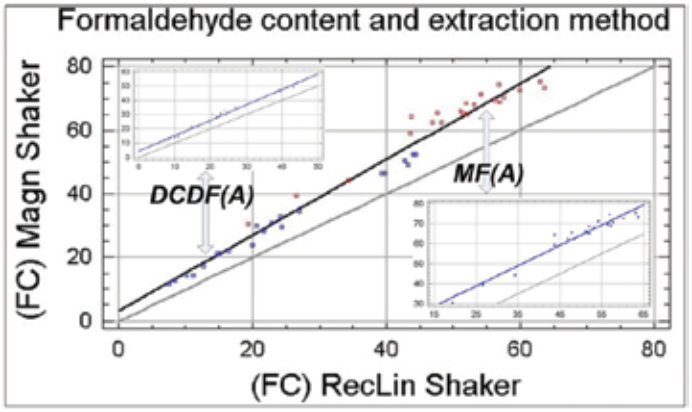

Figure 4. Linear regression relating formaldehyde contents obtained after extraction with magnetic shaker and reciprocal linear shaker of leather samples treated with MF (A) and DCDF (A) resins.

Influence of the Resin Type (MF and DCDF) of Low Formaldehyde Content

The comparison between resins of low formaldehyde content MF(A) and DCDF(A) was carried out using equations a and d. The combined regression is as follows:

MF(A)&DCDF(A): $FC_{MS} = 5.01 + 1.12 \times FC_{RLS}$ r = 0.976

The application of the method described by R. Mead[18] enables us to determine the signification level of the differences between MF (A) and DCDF (A):

Source of variation	RSS	df	s^2	$F_{2.38}$	Signification level
Combined MF(A) & DCDF(A)	408.38	40			
Individual MF(A) + DCDF(A)	191.01	38	5.03		
Combined – MF(A) – DCDF(A)	217.37	2	108.69	21.6	1%

Figure 4 shows the formaldehyde content in leather samples treated with formaldehyde-based resins (MF and DCDF) of low formaldehyde content as a function of the agitation method used in the extraction phase.

The relationship between methods significantly depends on the type of resin. Results of MF (A) are generally higher and more dispersed than those of DCDF (A). Extraction with magnetic shaker gives higher formaldehyde contents than when reciprocal linear shaker is used and differences between methods are generally greater for melamine-formaldehyde resin, although a higher dispersion in the results is observed.

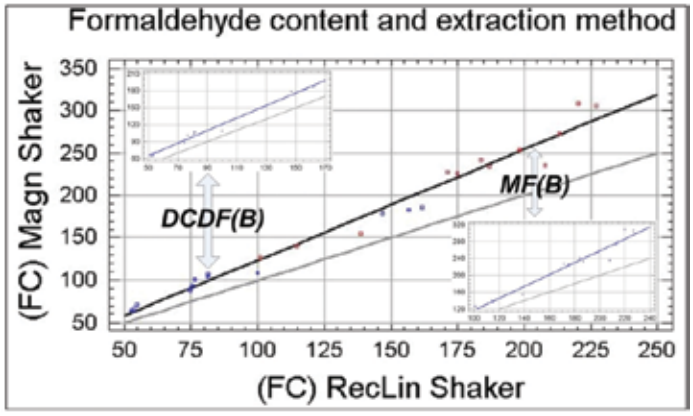

Figure 5. Linear regression relating formaldehyde contents obtained after extraction with magnetic shaker and reciprocal linear shaker of leather samples treated with MF (B) and DCDF (B) resins.

Influence of the Resin Type (MF and DCDF) of High Formaldehyde Content

Similar comparison can be done with resins of high formaldehyde content MF(B) and DCDF(B) using the regression equations b and e. The combined regression is the following:

MF(B)&DCDF(B): $FC_{MS} = -6.86 + 1.30 \times FC_{RLS}$ r = 0.987

By applying the method described by R. Mead[18], it is possible to determine the signification level of the differences between MF (B) and DCDF (B):

Source of variation	RSS	df	s^2	$F_{2.20}$	Signification level
Combined MF(B) & DCDF(B)	3533.13	22			
Individual MF(B) + DCDF(B)	2601.84	20	130.09		
Combined – MF(B) – DCDF(B)	931.29	2	465.65	3.58	5%

Figure 5 shows the formaldehyde content in leather samples treated with formaldehyde-based resins (MF and DCDF) of high formaldehyde content as a function of the agitation method used in the extraction phase.

Formaldehyde contents in splits treated with MF (B) resin are generally greater than those treated with DCDF (B) resin and the relationship between the two agitation methods significantly depends on the type of resin. When magnetic shaker is used, higher formaldehyde contents are obtained when compared with the reciprocal linear one. Differences between agitation methods are greater and more disperse when melamine-formaldehyde (B) resin is employed, and the greater the formaldehyde content, the higher the differences between methods. As for dicyandiamide-formaldehyde (B) resin, lower differences between the agitation methods are observed although a stronger linear relationship between them exists.

Influence of the Vegetable Compounds on the Linear Regression Between the Formaldehyde Content of Leather Samples Extracted by the Two Agitation Methods

The linear regressions of the samples with no vegetable compounds (reference) and those additionally treated with mimosa, quebracho and tara are the following:

REFERENCE: $FC_{MS} = -6.45 + 1.32 \times FC_{RLS}$ r = 0.994

MIMOSA: $FC_{MS} = 5.60 + 1.15 \times FC_{RLS}$ r = 0.995

QUEBRACHO $FC_{MS} = 4.29 + 1.19 \times FC_{RLS}$ r = 0.996

TARA $FC_{MS} = -3.14 + 1.31 \times FC_{RLS}$ r = 0.998

Intercept and slope values of the regression equations suggest similarities between “reference” and “tara” by one side and “mimosa” and “quebracho” by the other.

The results of the comparison between all possible pairs of regressions are the following:

“Reference” and “Mimosa”

Source of variation	RSS	Df	s^2	$F_{2.32}$	Signification level
Combined REFERENCE & MIMOSA	2632.40	34			
REFERENCE + MIMOSA	2000.17	32	62.51		
Combined – REFERENCE – MIMOSA	302.41	2	151.21	2.42	Non-significant

“Reference” and “Quebracho”

Source of variation	RSS	Df	s^2	$F_{2.32}$	Signification level
Combined REFERENCE & QUEBRACHO	3177.15	34			
REFERENCE + QUEBRACHO	2494.91	32	77.97		
Combined – REFERENCE – QUEBRACHO	682.24	2	341.12	4.38	5%

“Reference” and “Tara”

Source of variation	RSS	Df	s^2	$F_{2.26}$	Signification level
Combined REFERENCE & TARA	1968.84	28			
REFERENCE + TARA	1929.09	26	74.20		
Combined – REFERENCE – TARA	39.75	2	19.88	0.27	Non-significant

"Mimosa" and "Quebracho"

Source of variation	RSS	Df	s^2	$F_{2.32}$	Signification level
Combined MIMOSA & QUEBRACHO	1134.89	34			
MIMOSA + QUEBRACHO	1099.56	32	34.36		
Combined – MIMOSA – QUEBRACHO	35.33	2	17.67	0.51	Non-significant

"Mimosa" and "Tara"

Source of variation	RSS	Df	s^2	$F_{2.26}$	Signification level
Combined MIMOSA & TARA	974.37	28			
MIMOSA + TARA	533.74	26	20.53		
Combined – MIMOSA – TARA	440.63	2	220.32	10.73	1%

"Quebracho" and "Tara"

Source of variation	RSS	Df	s^2	$F_{2.26}$	Signification level
Combined QUEBRACHO & TARA	1475.90	28			
QUEBRACHO + TARA	1028.48	26	39.56		
Combined – QUEBRACHO – TARA	447.42	2	223.71	5.65	1%

The results of the comparisons confirm that the relationship between agitation methods of samples treated with "tara" is not significantly different from that of the "reference" samples (without vegetable compound) and that samples treated with "mimosa" and "quebracho" also show non-significant differences between regressions relating both agitation methods. Although there is a non-significant difference between "reference" and "mimosa", the results of the comparisons show that there is more similarity between "reference" and "tara" than "reference" and "mimosa".

Consequently linear regressions of "reference & tara", "mimosa & quebracho" and the combined regression of "Reference & tara" and "Mimosa & Quebracho" are determined:

REFERENCE & TARA: $FC_{MS} = -5.07 + 1.32 \times FC_{RLS}$ r = 0.996

MIMOSA & QUEBRACHO: $FC_{MS} = 4.56 + 1.18 \times FC_{RLS}$ r = 0.996

"Reference & Tara and "Mimosa & Quebracho: $FC_{MS} = 0.002 + 1.26 \times FC_{RLS}$ r = 0.995

The application of the method described by R. Mead[18] enables us to determine the signification level of the differences between "REF&TARA" and "MIM&QUEB":

Source of variation	RSS	Df	s^2	$F_{2.62}$	Signification level
Combined REF & TARA and MIM & QUEB	4188.25	64			
REF & TARA + MIM & QUEB	3103.73	62	50.06		
Combined – REF & TARA- MIM & QUEB	1084.52	2	542.26	10.83	1%

Figure 6 shows the formaldehyde content in leather samples treated only with formaldehyde-based resins or jointly treated with tara powder vs. that of samples jointly treated with formaldehyde-based resins and mimosa or quebracho extracts as a function of the agitation method used in the extraction phase.

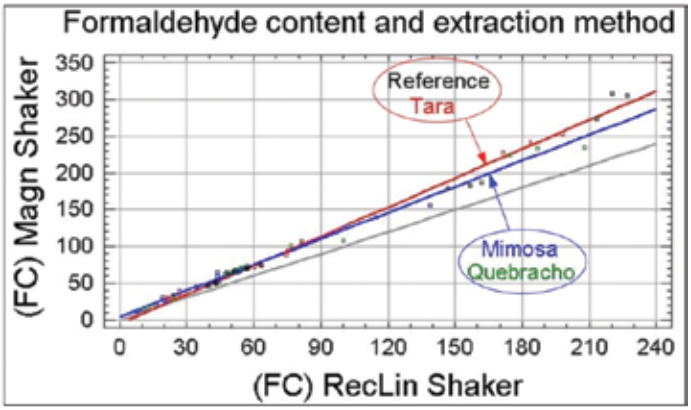

Figure 6. Linear regression relating formaldehyde contents obtained after extraction with magnetic shaker and reciprocal linear shaker of leather samples treated only with formaldehyde-based resins or jointly treated with tara powder and of samples treated with formaldehyde-based resins together with mimosa or quebracho extracts.

The two linear regressions are very significantly different. It can be observed that results corresponding to the formaldehyde content of "reference & tara" obtained by magnetic shaker are higher than those of "mimosa & quebracho" especially for high values of formaldehyde content. At higher formaldehyde content, samples treated with mimosa or quebracho gave more similar results between the two methods, than those non treated with vegetable compound ("reference" samples) or treated with "tara". It seems that magnetic shaking favors the extraction of formaldehyde from samples with no vegetable compound or containing "tara". As observed, magnetic shaking leads to greater formaldehyde content than reciprocal linear shaking.

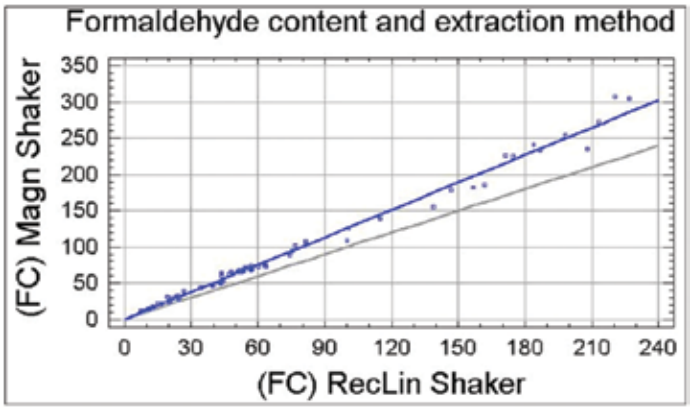

Figure 7. Linear regression relating formaldehyde contents obtained after extraction with magnetic shaker and reciprocal linear shaker of leather samples treated with formaldehyde-based resins with and without vegetable compounds.

Table III
Number of analyses that meet (reciprocal linear shaker) and meet or fail (magnetic shaker) with respect to allowable limits in formaldehyde content. Fail percentage of magnetic shaker vs. reciprocal linear shaker.

Levels of FC Allowable Limits	Shaking Method			Fail % in MS vs. RLS
	Rec.Lin. Shaker	Magnetic Shaker		
		fail	meet	
20 mg/kg	10	5	5	50.0
50 mg/kg	19	9	10	47.4
75 mg/kg	17	3	14	17.7
250 mg/kg	20	5	15	25.0
Total	66	22	44	**33.3**

FC: Formaldehyde content; **MS**: Magnetic shaker;
RLS: reciprocal linear shaker

From the regression coefficients of equations m and n, it can be said that formaldehyde content in "reference" samples (without vegetable compounds) or treated with "tara" is 32% higher (**equation m**) when using magnetic shaker instead of the reciprocal linear one while for samples treated with mimosa or quebracho extracts, the formaldehyde contents after magnetic shaking are 18% greater (**equation n**) than those obtained when using reciprocal linear shaking in the extraction phase.

Influence of the Shaking Methods on the Formaldehyde Content of Samples Treated with Formaldehyde-based Resins with and Without Vegetable Compounds

When all the treatments are considered (**equation o**), magnetic shaking leads to formaldehyde contents that are 26% greater than those obtained with the reciprocal linear one.

The application of the t-test[19] reveals non-significant differences between the intercept (0.002) and zero. Consequently, results of the formaldehyde content after magnetic shaking can be related to those after reciprocal linear shaking by fitting a straight line with no intercept, as follows:

$$FC_{MS} = 1.26 \times FC_{RLS} \qquad r = 0.998$$

Figure 7 shows the formaldehyde content in leather samples treated with formaldehyde-based resins with and without vegetable compounds as a function of the agitation method used in the extraction phase.

In general, when using magnetic shaker of the type considered in this work in the extraction of formaldehyde from leather treated with formaldehyde-based resin with/without vegetable compounds provides formaldehyde contents, which are 26% greater than when extraction is carried out with the reciprocal linear shaking.

Influence of the Shaking Method on Failure/acceptance of Formaldehyde Content Results in Relation to Allowable Limits

The results of formaldehyde content using magnetic shaker are higher than those obtained with the reciprocal linear shaking method. The experimental results of Table 2 obtained with the reciprocal linear shaking method have been classified in accordance with their formaldehyde content. Table III shows the number of analyses of the formaldehyde content obtained with the reciprocal linear shaker that met the different allowable limits (66 analyses in total). Table III also shows, for each level of allowable limits and for the same samples as for the reciprocal linear shaker, the number of analyses whose

results of the formaldehyde content obtained with the magnetic shaker fail or meet these limits. The percentage of fails given by the magnetic shaking method vs. the reciprocal linear one is also presented in Table II.

The magnetic shaking method yielded one-third (22 out of 66) of the results in the formaldehyde content exceeding the limits that were fulfilled by the reciprocal linear shaking one. The lower the allowable limits the higher the percentage of fails approaching to the half of the determinations. The situation urges the clarification of the shaking method in the EN ISO 17226 Standard to avoid the high level of contradictory results provided by the two methods (taken as examples) considered in this work and that fulfill the sentence "***Stir*** *or* ***shake smoothly*** the content of the flask" in the initial phase of the Standard for formaldehyde extraction.

Conclusions

Magnetic shaking used in the extraction of formaldehyde from leathers treated with formaldehyde-based resins with and without vegetable compounds leads to formaldehyde contents which are 26% greater than those obtained when using the reciprocal linear shaking method.

The shaking method used in the extraction phase of formaldehyde from leather samples influences on the formaldehyde content in these samples and differences between shaking methods are slightly modified by the formaldehyde-based resins and vegetable compounds applied. Formaldehyde content of reference samples (without vegetable compounds) or treated with tara powder was 32% higher when magnetic shaking was used in the extraction phase instead of reciprocal linear shaking while the increase was of 18% in the formaldehyde analysis of leather samples treated with mimosa or quebracho extracts. This could be related with the lower content of formaldehyde observed in samples treated with these vegetable compounds.

Taking as reference the different allowable limits in formaldehyde content included in the "restricted substances list" of major brands, the use of the magnetic shaker for the extraction of formaldehyde from leather failed in one-third of the examined samples that when using the reciprocal linear shaker would be fulfilled. The high ratio of disagreement between the two methods, which fulfill the EN ISO 17226 Standard (Parts 1 and 2), makes urgent the modification of the sentence "Stir the content of the flask or shake smoothly at 40°C ± 0.5°C in a water bath for 60 min ± 2 min" included in the text, in order to specify more clearly the type of agitation to be used in the extraction phase of formaldehyde from leather.

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References

1. Carlson, R.M., Smith M.C. and Nedorost S.T.; Diagnosis and treatment of dermatitis due to formaldehyde resins in clothing. *Dermatitis* **15**, 169-175, 2004.
2. IARC (International Agency for Research on Cancer) Monographs. *Chemical Agents and Related Occupations* **100F**, 401-435, 2012.
3. Dixit, S., Yadav, A., Dwivedi, P.D. and Das, M.; Toxic hazards of leather industry and technologies to combat threat: a review. *J. Clean. Prod.* **87**, 39-49, 2015.
4. Naviglio, B., Calvanese, G., Tortota, G., Cipollaro, L. and Pierri.; Characterization of tannery chemicals: Retanning agents. *Cuoio Pelli Materie Concianti*, **82**(2), 83-102, 2006.
5. Barret, R. McD. Amino resins in Surface Coatings. Volume 1. Part 1. Raw materials and Their Usage. Ed. Chapman & Hall, London 3rd Edition, 134-145, 1993.
6. Font, J., Viera, S., Rius, T., Reyes, M., Jorba, M., Verdú, E., Juárez, M. A., Cuadros, S. and Marsal, A.; Inter-Laboratory Study on Formaldehyde: Determination by HPLC. *JALCA* **103**, 53-61, 2008.
7. Bacardit, A., van der Burgh, S., Armengol, J. and Ollé, Ll.; Evaluation of a new environment friendly tanning process, *J. Clean. Prod.* **65**, 568-573, 2014.
8. Thanikaivelan, P., Mohan, C.R., Saravanabhavan, S., Rao, J.R. and Nair, B.U.; Development of Formaldehyde-free Leathers in Perspective of Retanning. Part 1: Benchmarking for the Evolution of a single Syntan System. *JALCA* **102** (10), 306-314, 2007.
9. Mohan, C. R., Saravanabhavan, S., Thanikaivelan, P., Rao, J. R. and Nair, B.U.; Development of Formaldehyde-free Leathers in the Perspective of Retanning. Part II: Combination of formaldehyde-free retanning syntans. *Clean Technol. Environ. Policy* **10**, 287-294, 2008.
10. A3 Chair in Leather Innovation of the Universitat Politècnica de Catalunya. Internal Report of Activities. Igualada, 2016 (unpublished work)
11. EN ISO 17226-1 Standard: "Determination of formaldehyde content in leather. Part 1. Quantification by HPLC," 2008.
12. EN ISO 17226-2 Standard: "Determination of formaldehyde content in leather. Part 2. Quantification by colorimetric analysis," 2008.

13. EN ISO 17226-3 Standard: "Determination of formaldehyde content in leather. Part 3. Formaldehyde emissions from leather," 2011.
14. Cuadros, S., Font, J., Izquierdo, F., Cuadros, R.M., Ollé, Ll. and Marsal, A.; Determination of formaldehyde content in leather: Standard EN ISO 17226 (Parts 1 and 2), revision and possible improvements, *J. Soc. Leather Technol. Chem.* **100**, 167-174, 2016.
15. Marsal, A., Cuadros, S., Manich, A.M., Izquierdo, F. and Font, J.; Reduction of formaldehyde content in leathers treated with formaldehyde resins by means of plant polyphenols, *J. Clean. Prod.* **148C**, 518-526, 2017. DOI: 10.1016/j.jclepro.2017.02.007
16. EN ISO 2419 Standard: "Sample preparation and conditioning," 2012.
17. EN ISO 14088 Standard: "Quantitative analysis of tanning agents by filter method", 2012.
18. Mead, R., Curnow, R.N. and Hasted A.M.; Statistical Methods in Agriculture and Experimental Biology, 3rd ed. Chapman & Hall/CRC (Boca Raton, Florida). 245 – 250, 2003
19. Mead, R., Curnow, R.N. and Hasted A.M.; Statistical Methods in Agriculture and Experimental Biology, 3rd ed. Chapman & Hall/CRC (Boca Raton, Florida). 189 – 190, 2003