

Alternative Method to Determine the Free Formaldehyde Content in Leather

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Abstract

Formaldehyde might possibly be available in some chemical auxiliaries such as biocides, syntans, amino resins, fatliquors, dyeing auxiliaries and finishing products. It is considered as a toxic substance, with irritant and local necrotic effects and potentially carcinogenic because of high chemical reactivity and versatility as a chemical intermediate. Its health risks give rise to scrutinize the existence and possible formation of formaldehyde in leather as well as all the articles in daily uses.

Free or releasable formaldehyde in leather are of main importance to insist on the determination in the ecological viewpoint. The formaldehyde content of leather is analyzed by high performance liquid chromatography (HPLC) method that utilize the analytical chemical 2,4 dinitrophenyl hydrazine (DNPH). However, analyte from the samples interfere with numerous substances after derivatization DNPH. The aim of the present study was to develop a selective and sensitive method for the quantitation of formaldehyde in the leather samples. The method by using headspace device adapted to gas chromatographic/mass spectrometry (HS-GC/MS) was performed to determine formaldehyde with derivatization *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA).

Key words: Formaldehyde, Leather, Head space-GC/MS, *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine.

Introduction

Formaldehyde is a colorless, strong smelling chemical compound widely used in many industries such as automobile, textile, cosmetic, agriculture, mining, leather etc. It is the simplest member of aldehyde chemically with the formula HCOH. Formaldehyde is a gas at room temperature, but it is also readily soluble in water. It might possibly be available in some chemical auxiliaries such as biocides, syntans, amino resins, fatliquors, dyeing auxiliaries and finishing products. Other alternative tanning options can be polyphenols, oxazolidine, formaldehyde, polymers, carbohydrates, etc(1). It is considered as a toxic substance, with irritant and local necrotic effects and potentially carcinogenic because of high chemical reactivity and versatility as a chemical intermediate. Its health risks give rise to scrutinize the existence and possible formation of formaldehyde in leather as well as all the

articles in daily uses. Free or releasable formaldehyde in leather are of main importance to insist on the determination in the ecological viewpoint.

The aim of the study is to develop a selective and sensitive method for the quantitation of formaldehyde in the leather samples. The findings indicate that this method allows for accurate analysis that proves useful assessing formaldehyde content of leather.

Material and Method

Material

Eight pickled conserved sheep skins from New Zealand origin were used for the study. The skins were divided two groups which are blank and formaldehyde applications. Same recipe was applied for all skin samples until tanning process and then classified to the two pieces. Formaldehyde which is technical grade (Merck) was used at three different proportions as a tanning agent.

Method

All leather samples were applied in accordance with the recipe given in the Table 1. Aldehyde was not used for control group skins.

Table 1. Recipe which was applied for the study.

Process	%	Material	°C	Time	pH
De-pickling	200	6 °Be Brine	25		
	+1	Sodium formate		15'	
	+0.8	Sodium carbonate		45'	5.0
Bating	100	Water			
	+1	Enzyme 1000 LVC		60	
Washing	100	Water		15	
Degreasing	4	Nonionic surface active		60	
Washing	150	3 °Be Brine		15*3	
Pickling and Tanning	75	2 °Be Brine	25		
	+1	Sulphonic acid			
	+2	Synthetic fatliquoring (1:5)	30		
	0.8	Formic acid (1:10)			3.5
	X	Formaldehyde			
	+2	Basic chromium sulphate			
	+1	Synthetic tannin			
	+1	Sodium formate			
	+0.5	Sodium bicarbonate			
	+1	Anionic resin			

Preparation of the leather samples for analysis

The leather sample was grounded and then, conditioned according to the IUC 3 standard (2).

Formaldehyde analysis by HPLC

The samples were extracted in accordance with the IUC 19 (3) standard method for determination of formaldehyde. For this, 2.0 ± 0.1 g of leather grounded was extracted with 50mL of 0,1 % sodium dodecyl sulphanate solution. The formaldehyde content of leather is analyzed the method that utilize the analytical chemical 2, 4 dinitrophenyl hydrazine (DNPH). However, analyte from the samples interfere with numerous substances after derivatization of DNPH. Agilent 1200 HPLC system was used consisting of diode array and multiple wavelength detectors. Samples were injected with an auto-sampler with a 20 mL sample.

Table 2. Operational conditions of HPLC

Column	ZORBAX Eclipse XDB-C18 4.6x150mmx5 μ m with pre-column
Mobile Phase	Acetonitrile/W 60/40
Flow rate	1 mL/min
UV detection wavelength	350nm

Formaldehyde analysis by Gas Chromatography Mass Spectrometry with Head Space (HS-GC/MS)

The headspace gas chromatographic with the mass spectrometry (HS-GC/MS) method was performed to determine formaldehyde with derivatization o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA) (4,5,6). According to the method, 1 mL of this solution, 120 μ L PFBOA(1mg/mL), and 0,6g NaCl were added in the head space vials. A 7694 E model Head Space (Agilent) device was connected to 5975C/7890A model GC/MS (Agilent) in the study. The conditions of the head space and GC-MS systems were given in Table 3 and Table 4.

Table 3. Operational conditions of GC/MS and Head Space

GC-MS	
Column	HP-5/Supelco 2380 Fused silica capillary column 30mx0,25mx0,2 μ m
Oven Temperature	80°C (2min) \rightarrow 7°C/min \rightarrow 150 °C \rightarrow 15°C \rightarrow 220°C
Carrier gas	He 16 psi
Injection temperature	200 °C
Head Space Auto Sampler	
Vial Equilibration time	24 min.
Vial Temperature	80 °C
Transfer temperature	120 °C
Pressurization time	1 min
Pressure of helium	14 psi
Injection time	1 min

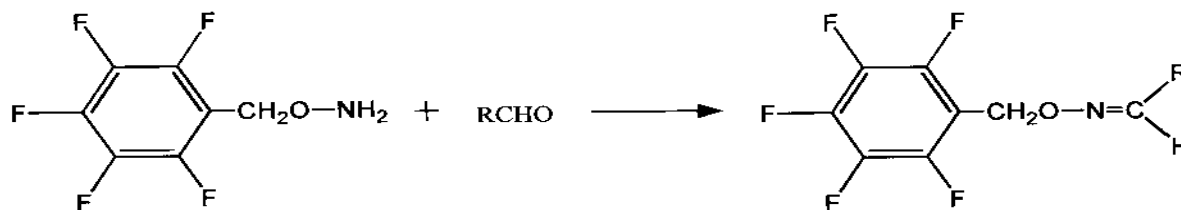


Figure 1. General reaction of an aldehyde with PFBOA(o-(2 ,3,4,5,6-pentafluorobenzyl)-hydroxylamine).

Variation of PFBOA concentration showed that peak height for $50\mu\text{g/L}^{-1}$ HCOH increased until 0,8mg/2mL although 1,2mg/2mL selected for higher concentrations of HCOH

It is known that head space sampling methods are very useful for determination volatile organic compounds, and the addition of NaCl is available for enhancing the sensitivity (6). Upon increasing NaCl concentration in the vial containing $50\mu\text{g/L}^{-1}$ HCOH a gradual increase in the peak height was observed (Table 4). The solubility of NaCl is limited to solubility Ca 0.7 g.2mL^{-1} , so 0.6g was chosen.

Table 4. The effect of PFBOA and NaCl concentrations on effect of the analysis

Amount of PFBOA mg/2mL	Peak Height	Amount of g NaCl/ 2mL	Peak Height
0.08	4555	-	2746
0.4	5646	0.1	5811
0.8	6444	0.4	5844
1.2	6442	1.6	6442

Table 5. Comparison of HCOH results from different leather samples obtained by Head Space-GC/MS and HPLC method.

Sample name	Mean value of HCOH by HPLC method (mgkg^{-1})	Mean value of HCOH by HS GC MS method (mgkg^{-1})
1	9.6	4,8
2	10.8	3,9
3	5.3	6.5
4	19.9	5,5
5	11.0	6,7
6	5.1	4,3
WB	0.8	0,2
F/WB a	2.7	0,5

Results

Satisfactory results were obtained in comparison to the standard method and the method used was proved to be an alternative way for sensitive and selective determination of formaldehyde in different leather samples and potential interference of extraction solutions. Formaldehyde contents of the leathers were found higher than the value obtained from the head space GC-MS system. It is thought that the chemical DNPH used in the HPLC method has high reactivity to the other aldehyde and ketone groups.

References

- (1) Covington, A. D., 2008, Alternative Tanning Options. Leather Magazine, July, 16-22.
- (2) ISO 4044 (EN ISO 4044), 2008, Preparation of chemical test samples (IUC 3).
- (3) ISO 17226-1 (EN ISO 17226-1), 2008, Determination of formaldehyde content in leather Part 1: Quantification by HPLC (IUC 19-1)
- (4) Kanagaraj, J., Sadulla, S., Jawahar, M., Babu, K., 2002, *Interaction Of Aldehyde Developed From Amino Acids Of Tannery Waste In A Lowerchrome Tannage: An Eco-Friendly Approach*, Journal of the Society of Leather Technologists and Chemists, vol 86, p.18, India
- (5) Nishikawa, H. ve Yasuhara, A., 1995, Derivatization and Gas Chromatographic or High Performance Liquid chromatographic Analysis of Aldehydes in Air Samples., *J. of Environmental Chemistry*, 5, 199–205.
- (6) van Leeuwen, S. M., Hendriksen L., Karst, U., 2004, Determination of aldehydes and ketones using derivatization with 2,4-dinitrophenylhydrazine and liquid chromatography–atmospheric pressure photoionization–mass spectrometry, *Journal of Chromatography A*, Volume 1058, Issues 1-2, 26 November 2004, Pages 107-112