Determination of Free Formaldehyde in Leather Chemicals

by

Yudan Yi,[1] Wei Ding,[1] Ya-nan Wang,[1,2]* and Bi Shi[1,2]

[1]*National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University,* Chengdu 610065, China

[2]*Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education,* Chengdu 610065, China

Abstract

Formaldehyde is widely used in the synthesis of various leather chemicals due to its high reactivity and low cost. It is probably introduced into leather when applying the chemicals to processing, and then released during storage and use of leather, which may pose a potential risk to human health. Existing method for determining formaldehyde in leather is helpless to deal with the complicated chemicals. In this study, a method was optimized for determination of free formaldehyde in leather chemicals based on ISO 27587. A 0.5-2.0 g sample of leather chemical (formaldehyde could range from 1.25 to 1250 mg/kg) was heated at 90 °C in nitrogen atmosphere. The released formaldehyde was purged at a flow rate of 300 mL/min for 30 min, captured and derivatized using a bubble absorption tube containing 2,4-dinitrophenylhydrazine absorption solution, and then detected by HPLC-diode array detector. The recovery rate of formaldehyde standard solution was 91.0% with relative standard deviation (RSD) of 4.87% in seven times repeated trials. The repeated determinations of aldehyde tanning agents showed the formaldehyde recoveries higher than 90% and RSD lower than 7%, indicating the accuracy and precision of the method. Powdery amino resins were determined to contain a tiny amount of free formaldehyde using this method. However, it should be noted that hydrolyzed formaldehyde will be formed when the amino resins were dissolved in water and used in retanning, leading to the potential for bringing leather with high content of formaldehyde.

Introduction

Formaldehyde is one of the most essential basic materials for the synthesis of leather chemicals. Some chemicals widely used in chrome-free tanning and retanning, such as modified glutaraldehyde, oxazolidine, syntans and amino resins, are synthesized with formaldehyde.[1,2] The advantages of formaldehyde include high reactivity and low cost. However, it is generally hard to completely consume formaldehyde during synthesis, resulting in free/reversible formaldehyde remaining in the chemicals.[3] Consequently, formaldehyde is likely to be introduced into leather when the chemicals containing residual formaldehyde are used in leather processing. In fact, this is regarded as the main source of formaldehyde in leather.

Formaldehyde has been classified as one of the carcinogenic and teratogenic substances by World Health Organization (WHO).[4,5] European Chemical Agency (ECHA) has prioritized formaldehyde under Substances of Very High Concern (SVHC) which are deemed to be hazardous not only to the environment but to humans.[6] Therefore, many countries and organizations have established regulations to limit the content of formaldehyde in leather. For example, formaldehyde content of leather and fur products is limited to 20 mg/kg for products for babies (within 24 months), 75 mg/kg for products with direct contact to skin, and 300 mg/kg for products without direct contact to skin in the national standard of China.[7] Furthermore, the OEKO-TEX® standard 100 stipulates that the free formaldehyde and partially released formaldehyde should be undetectable in leather products for babies.[8] Since leather chemicals are the major source of formaldehyde in leather, the determination of free formaldehyde in leather chemicals is of great significance to evaluate the quality of leather chemicals, control the formaldehyde content of leather and ultimately ensure the ecological properties of leather products.[9,10]

The commonly used standard method for determination of formaldehyde in leather is ISO 17226-1. Formaldehyde in leather is first extracted by a detergent solution, then reacted with 2,4-dinitrophenylhydrazine (DNPH) and determined by HPLC.[11] The extraction method has been well developed and suitable for leather sample. However, it is difficult to accurately measure the formaldehyde in leather chemicals because complicated components were mixed together when a chemical

*Corresponding author email address: wangyanan@scu.edu.cn

Manuscript received April 10, 2019, accepted for publication June 27, 2019

was dissolved in aqueous phase. In this case, a dynamic diffusion method was established by TEGEWA-group. Free formaldehyde was purged with a stream of nitrogen gas, captured by a DNPH cartridge, and then analyzed by HPLC after elution in this method.[12] Unfortunately, some parameters, such as flow rate of nitrogen and sampling amount, were not mentioned. Based on the method above, ISO 27587-2009 was then published to quantitatively determine free formaldehyde in leather process auxiliaries.[13] However, some details during the gas-phase extraction were not specified yet. What's more, the DNPH cartridge employed in this method was high in cost and not easily available for routine analysis. Therefore, it is still necessary to further improve this method. The aim of this work is to propose a more practical method on the basis of the existing method. DNPH cartridge was replaced by DNPH absorption solution for the sake of cost saving and convenience. Moreover, extraction conditions, including flow rate of nitrogen, incubation temperature and purging time, were optimized in order to establish an accurate and precise method for determining free formaldehyde in a variety of leather chemicals.

Experimental

Materials

Certified reference material of formaldehyde in water (GBW(E) 081701, 100 μg/mL) was purchased from Beijing Hongmeng Reference Material Technology Co. Ltd., China. HPLC-grade acetonitrile and 2,4-dinitrophenylhydrazine (DNPH) cartridges were purchased from Sigma-Aldrich Co. LLC. The other agents used for analysis were of analytical grade. Five aldehyde tanning agents (aqueous solution, labeled as A, B, C, D and E) were prepared in our laboratory. Four amino resins (powder, labeled as 1#, 2#, 3# and 4#) were obtained from leather chemicals companies. 1# and 2# were dicyandiamide-formaldehyde resins, and the other two were melamine-formaldehyde resins. Bovine wet blue leather (shaved to the thickness of 1.5 mm) was provided by a local tannery. All the chemicals used for leather processing were of commercial grade.

Determination of Formaldehyde in Leather Chemicals

Formaldehyde in leather chemicals was determined mainly in accordance with the standard ISO 27587-2009,[13] and some modifications were made. Extraction of formaldehyde from the chemicals was conducted first. As shown in Figure 1, nitrogen cylinder, flow meter, U-tube and bubble absorption tube were connected in sequence by silicone tubing. A sample was put into the U-tube and was incubated at a certain temperature. Free formaldehyde in the sample was purged by nitrogen gas and was collected by 25 mL DNPH absorption solution in the bubble absorption tube. It should be noted that DNPH absorption solution, instead of the DNPH cartridge used in ISO 27587, was prepared by mixing 0.3wt% DNPH solution (dissolving 0.3 g DNPH in 99.7 g concentrated phosphoric acid), acetonitrile and distilled water in the volume ratio of 1:8:11.

Then the absorption solution was transferred to a 50 mL volumetric flask and diluted with fresh DNPH absorption solution. After standing in the dark for 30 min to 150 min, it was filtered through a 0.45 μm membrane filter and analyzed using High Performance Liquid Chromatography (HPLC, 1260 Infinity II, Agilent, USA) equipped with a CAPCELL PAK C_{18} MG II column (4.6mm × 150mm, Shiseido, Japan). The injection volume of sample was 20 μL. The eluent was the mixture of acetonitrile and distilled water (60%:40%, v/v) at a flow rate of 1.0 mL/min under 30°C. Then the target substance (formaldehyde phenylhydrazone) was detected by DAD at 360 nm.

Effects of Extraction Conditions on the Determination of Formaldehyde

In order to investigate the effects of extraction conditions, including flow rate of nitrogen, incubation temperature and purging time, on formaldehyde determination, 0.2 mL of

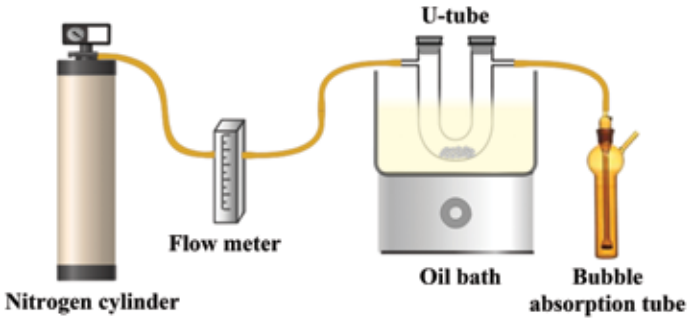

Figure 1. Schematic diagram of the formaldehyde extraction system.

Table I
L9 (3^3) orthogonal experimental design.

Level	(A) Temperature/ °C	(B) Flow rate/ (mL/min)	(C) Time/ min
1	70	200	20
2	80	250	30
3	90	300	40

formaldehyde standard solution (GBW(E) 081701) was pipetted as a sample to be tested. The recovery rate of formaldehyde was calculated by the following equation:

$$\text{Recovery rate (\%)} = (20\text{-}[FC])/20\times100 \quad (1)$$

where 20 is the theoretical formaldehyde content in formaldehyde standard solution (μg), *[FC]* is the formaldehyde content determined by HPLC (μg).

The flow rate of nitrogen was optimized first. It was adjusted to 100, 150, 200, 250, 300 and 350 mL/min, respectively. The incubation temperature was set to 90°C, and the purging time was 30 min. The other conditions were the same as the section above, and the recovery rate of formaldehyde was calculated. Then the effect of incubation temperature (60, 70, 80, 90 and 100°C, respectively) on formaldehyde determination was investigated. Nitrogen flow rate was set to 300 mL/min, and the purging time was 30 min. With regards to the optimization of purging time, the system was purged with nitrogen at 90°C and a flow rate of 300 mL/min for 20, 30, 40, 50 and 60 min, respectively.

According to the results of single-factor experiment, orthogonal test was performed. The recovery rate of formaldehyde was used as the evaluation index. The flow rate of nitrogen, incubation temperature and purging time were considered as three factors, and Table I represents L9 (3^3) orthogonal level list.[14]

Table II
Post-tanning processes.

Process	%	Chemical	°C	Time	pH/remarks
Rewetting	200	Water	35		
	0.2	Non-ionic degreasing agent			
	0.2	Formic Acid		40 min	pH 4.0, Drain
Neutralization	100	Water	35		
	1.5	Sodium Formate			
	0.2	Sodium Bicarbonate		15 min	
	0.2	Sodium Bicarbonate		15 min	
	0.2	Sodium Bicarbonate		45 min	pH 6.0, Drain
Washing	400	Water		10 min	
Retanning	100	Water	40		
	5	Amino Resin		60 min	
	0.2	Formic Acid		15 min	
	0.2	Formic Acid		15 min	
	0.2	Formic Acid		45 min	pH 4.0
Fatliquoring	100	Water	50		
	6	Fatliquoring agent			
	0.2	Formic Acid		30 min	pH 3.8, Drain

Effect of Derivative Devices on the Determination of Formaldehyde

DNPH absorption solution, placed in a brown bubble absorption tube (with a sand core filter), was applied for formaldehyde capture and derivatization in this study. For comparison, a DNPH cartridge, which was loaded with a high purity silica adsorbent coated with 2,4-DNPH, was also used according to ISO 29587-2009. Formaldehyde contents in formaldehyde standard solution and three types of aldehyde tanning agents were determined using the two derivative devices. The other conditions were the same.

Determination of Formaldehyde in Amino Resin and Leather

Four powdery amino resins (1#-4#) were sampled for determining formaldehyde. Meanwhile, 10g/L amino resin aqueous solutions were prepared, and 0.2 mL was sampled and determined for formaldehyde content.

Wet blue leather was retanned by the four amino resins, respectively, according to the processes shown in Table II. The crust leathers were dried, conditioned and determined for formaldehyde content following ISO 17226-1-2008.[11] Additionally, retanning floats before and after retanning were sampled, and Total Organic Carbon (TOC) concentrations were determined by TOC analyzer (Vario TOC, Elementar, Germany). The uptake rate of amino resin was calculated according to the measured TOC values.

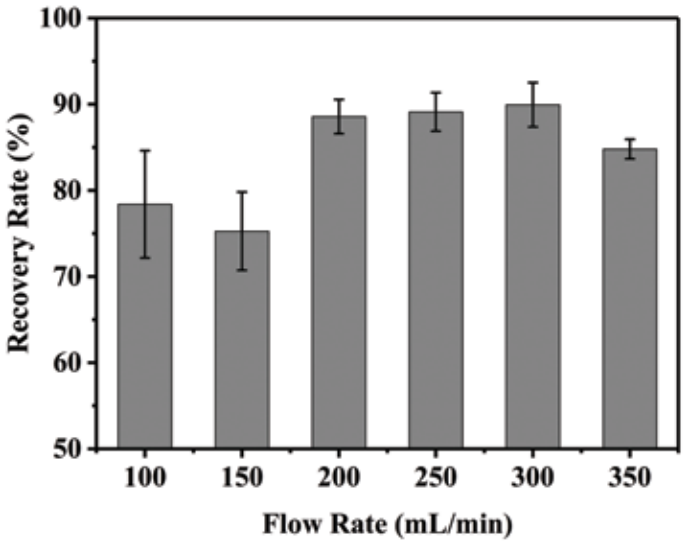

Figure 2. The effect of nitrogen flow rate on the recovery rate of formaldehyde.

Results and Discussion

Effect of Extraction Conditions on the Determination of Formaldehyde

Figure 2 shows the recovery rate of formaldehyde versus flow rate of nitrogen. In contrast to the low recovery rate (below 80%) at the nitrogen flow rate of 100-150 mL/min, the recovery rate of formaldehyde was over 88% when the nitrogen flow rate ranged from 200 to 300 mL/min. However, the recovery rate was decreased with the rise of nitrogen flow rate to 350 mL/min. Lower flow rate allowed the presence of more condensate on the

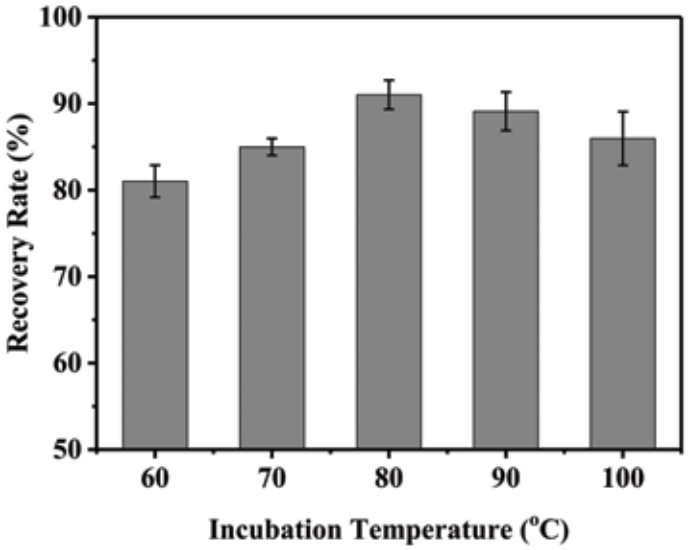

Figure 3. The effect of incubation temperature on the recovery rate of formaldehyde.

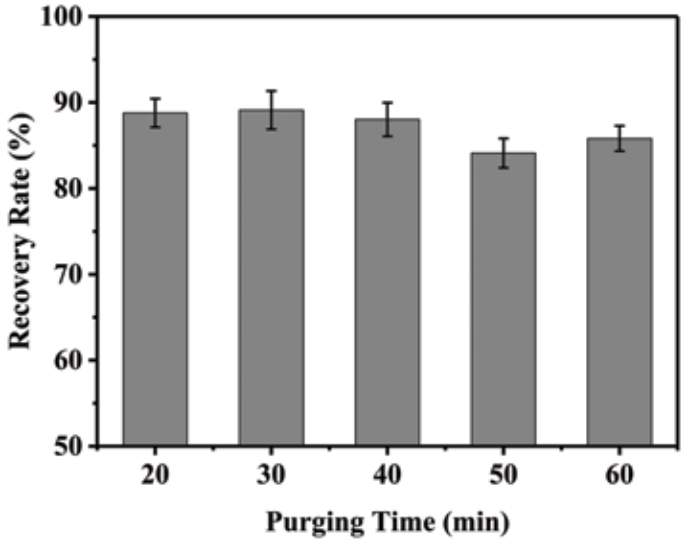

Figure 4. The effect of purging time on the recovery rate of formaldehyde.

wall of U-tube near the side of the bubble absorption tube. The escaped formaldehyde was likely to redissolve in the condensate, leading to the loss of the extracted formaldehyde, even though hairdryer was employed to remove the condensate as much as possible. On the other hand, higher flow rate would result in incomplete absorption of formaldehyde, and thus lower recovery rate. Therefore, it was appropriate to adjust the nitrogen flow rate to 200-300 mL/min.

Figure 3 illustrates the formaldehyde recovery rate at various incubation temperatures. The recovery rate was increased first and then decreased slightly when the temperature ranged from 60 to 100°C. Free formaldehyde in the standard solution was released and carried to the absorption solution with a stream of nitrogen gas at a relatively high temperature.[15] It can be inferred that incubation temperature lower than 70°C may be too low to volatilize most formaldehyde from the substrate. Nevertheless, the condensate would be accumulated when the temperature rose to 100°C, making it difficult for the subsequent evaporation of condensate by hairdryer. Consequently, the preferable temperature range was 70-90°C in terms of high recovery rate and convenience of operation.

Table III
L9 Analysis of ranges of orthogonal results.

Trial	A		B	C	Recovery rate of formaldehyde (%)
1	1	1	1	1	83.86
2	1	2	2	2	84.99
3	1	3	3	3	86.44
4	2	1	2	3	86.2
5	2	2	3	1	87.06
6	2	3	1	2	84.8
7	3	1	3	2	91.04
8	3	2	1	3	85.65
9	3	3	2	1	88.78
K_1	255.29	261.1	254.31	259.7	
K_2	258.06	257.7	259.97	260.83	
K_3	265.47	260.02	264.54	258.29	
k_1	85.10	87.03	84.77	86.57	
k_2	86.02	85.90	86.66	86.94	
k_3	88.49	86.67	88.18	86.10	
Range (Rj)	3.39	1.13	3.41	0.85	
Significance of factors	B>A>C				
Optimized results	$A_3B_3C_2$				

It can be observed from Figure 4 that the recovery rate of formaldehyde was higher than 88% when purging for 20-40 min. Extending purging time had a detrimental effect on the recovery rate. This result indicated a fast process for formaldehyde release from the sample. Hence, purging time was set to be 20-40 min at this stage.

Based on the results of single-factor analysis, a L9 orthogonal array of Taguchi's experimental design[14] for the control factors, nitrogen flow rate, incubation temperature and purging time was conducted. As shown in Table III, nitrogen flow rate was the most significant factor as its Range (Rj) was the highest. The significance of the above factors for the recovery rate of formaldehyde was as follows: B (nitrogen flow rate) > A (incubation temperature) > C (purging time). The optimal combination was $A_3B_3C_2$, viz. incubation temperature 90°C, nitrogen flow rate 300 mL/min, and purging time 30 min.

Validation Parameters of the Proposed Method

Validation parameters such as linearity, limits of detection and quantification, detection range, precision and accuracy were evaluated under the optimized conditions to validate the proposed method.

The calibration was performed through plotting a graph of the formaldehyde derivative peak area versus the concentration (µg/mL). Figure 5 shows that the calibration curve was linear (R^2=0.99991) in the formaldehyde concentration range of 0.05 to

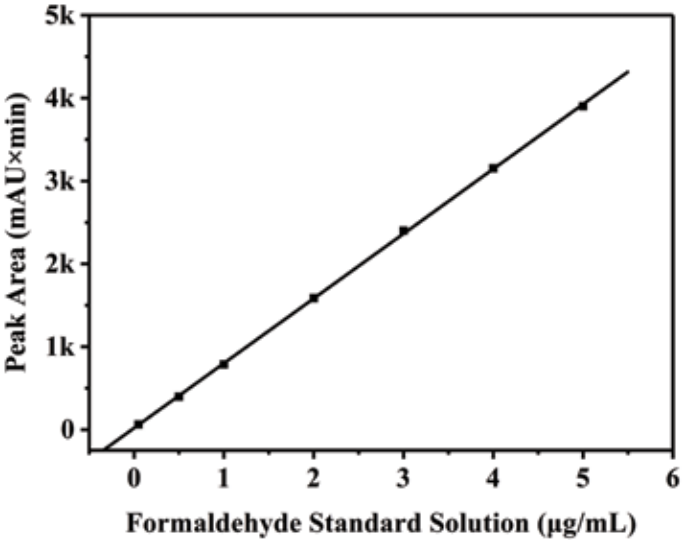

Figure 5. Standard curve of formaldehyde.

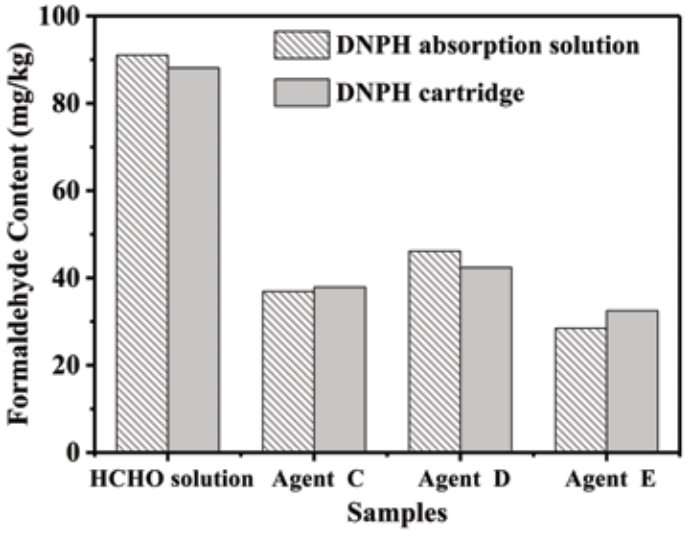

Figure 6. Effect of derivative devices on the determination of formaldehyde.

Table IV
Precision and accuracy of the method.

Agent	Test times	Average (µg/mL)	Recovery rate (%)	RSD (%)
Formaldehyde solution	7	91.02	91.0	4.87
Agent A	4	45.83	--	2.05
Agent B	4	842.12	--	1.92
Agent C	3	36.91	102.1	6.92
Agent D	3	46.16	90.0	2.21
Agent E	3	25.80	96.1	1.67

5.00 μg/mL, and the linear regression equation was Y=781.52X+20.35; N=7, where Y is the peak area in mAU × min, X is the formaldehyde concentration in μg/mL, N is the measured points. The limits of detection (LOD) serves as an indicator of the detectable concentration limits and is computed as three times the standard deviation of the regression divided by the slope of the calibration curve.[16] The LOD value for the HPLC method was 0.05 μg/mL. The limits of quantification (LOQ) value calculated as three times as LOD was 0.15 μg/mL. Considering the concentration range (0.05-5.00 μg/mL) of the calibration curve and the sampling mass of leather chemicals (0.5-2.0 g), the linearity range of the method was calculated as 1.25-1250 mg formaldehyde per kg of leather chemical. In other words, the method would be more reliable when the formaldehyde content of leather chemicals was between 1.25 mg/kg and 1250 mg/kg.

Precision, expressed as relative standard deviation (RSD), was evaluated by applying the proposed method to seven replicates of formaldehyde standard solution (100 μg/mL). The RSD was 4.87% as shown in Table IV. In addition, the RSDs of formaldehyde determination on five aldehyde tanning agents were all lower than 7%, suggesting a favorable repeatability of the proposed method.

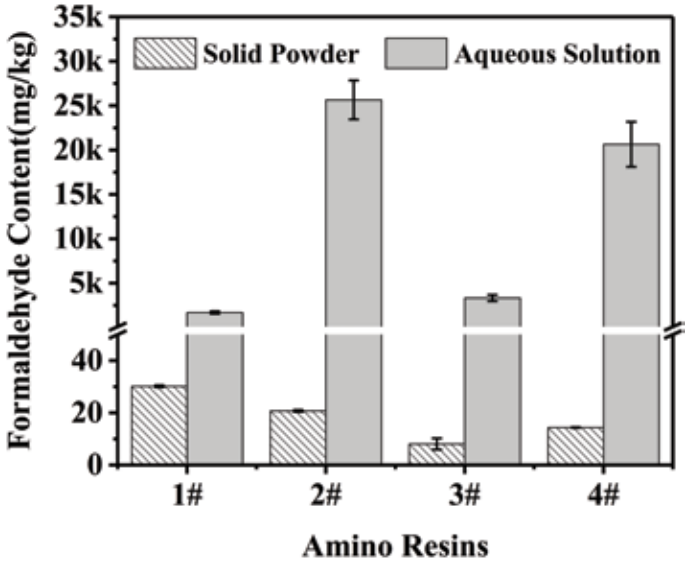

Figure 7. Formaldehyde content in powdery amino resins and their aqueous solutions.

Formaldehyde standard solution (100 μg/mL) was determined seven times according to the proposed method, and the average recovery rate was 91.0% (see Table IV). The formaldehyde recoveries of three aldehyde tanning agents (C, D and E) were also calculated by determining the analyte concentrations of both spiked and non-spiked samples. Satisfactory recoveries were achieved with the range of values between 90.0% and 102.1%, considering a range within the 80%-120% interval as an acceptable criterion.[17] Consequently, the accuracy of the analytical method was validated by the recoveries of formaldehyde standard solution and leather chemical samples.

Effect of Derivative Devices on the Determination of Formaldehyde

The derivative device used in ISO 27587 was DNPH cartridge, a commercial product. However, bubble absorption tube containing DNPH absorption solution was used as an alternative in this study in consideration of its convenience and lower cost. The influence of the different derivative devices on analysis of formaldehyde in leather chemicals was investigated using standard formaldehyde solution (100 μg/mL) and three aldehyde tanning agents (C, D and E) as samples. As can be seen from Figure 6, there were no obvious differences between the results using the two derivative devices. Therefore, bubble absorption tube containing DNPH absorption solution was capable of replacing DNPH cartridge to capture and react with the free formaldehyde.

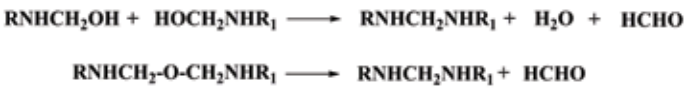

Figure 8. Reactions concerning formaldehyde release from amino resins.

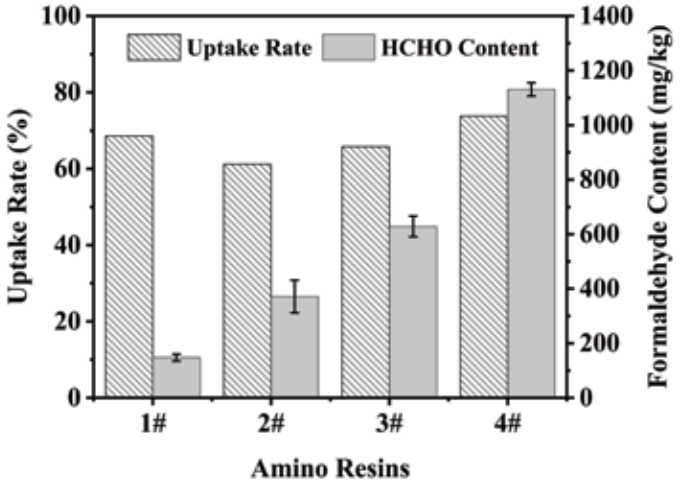

Figure 9. Uptake of amino resins and formaldehyde content in retanned leather.

Determination of Formaldehyde Content in Amino Resins and Retanned Leather

Figure 7 indicates that the free formaldehyde contents in powdery amino resins were all lower than 30 mg/kg, which was inconsistent with our common sense that amino resin is one of the main sources of formaldehyde in leather. In fact, most of the free formaldehyde in amino resin is volatilized under high temperature during spray drying of the preparation, resulting in low level of free formaldehyde in powdery product. Unlike in solid powder, formaldehyde in amino resin solution is much higher in content (all over 1500 mg/kg in Figure 7) and is easier to release because the condensation between amino monomers and formaldehyde is a reversible reaction. When amino resin was dissolved in water, the hydroxymethyl in the amino resin tended to break due to its high reaction activity, then a formaldehyde molecule was released (Figure 8).[18] Simultaneously, methylene ether groups would be formed at acidic conditions and then split under heating, leading to the increase in formaldehyde emission of amino resins (Figure 8). Hence, a humid and warm atmosphere was provided during extraction of amino resin solution, which contributed to the formation of the so-called hydrolyzed formaldehyde.

Similar conditions occurred in retanning of leather where amino resins were also applied in aqueous phase under heating. Undoubtedly, a large amount of formaldehyde was detected in the retanned leather (see Figure 9). As illustrated in Figure 7 and 9, the formaldehyde content in leather was not fully correspondence to its value in amino resin solution, which may be attributed to the different uptake rates of amino resin in retanning (Figure 9). As a result, the use of amino resins probably led to high formaldehyde content in leather even the free formaldehyde content of powdery amino resins was negligible determined by the proposed method in this study.

Conclusion

A method for determining free formaldehyde in leather chemicals was further developed on the basis of ISO 27587. Formaldehyde extraction conditions were optimized as follows. Nitrogen flow rate was 300 mL/min, incubation temperature was 90°C, and purging time was 30 min. Satisfactory accuracy (recovery rate > 90%) and precision (RSD < 7%) were achieved when bubble absorption tube containing DNPH absorption solution substituted for DNPH cartridge as the formaldehyde derivative device. Furthermore, this method had a wide measurement range and was enabled to determine formaldehyde in both solid and liquid samples with the merits of low cost and convenience. It was remarkable to note that powdery amino resins without much free formaldehyde determined by this method still pose a potential risk to high formaldehyde content in leather.

Acknowledgements

This work was financially supported by the National Key R&D Program (2017YFB0308500), Innovation Team Program of Science & Technology Department of Sichuan Province (2017TD0010) and Opening Project of Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education (20826041C4159).

References

1. Marsal, A., Cuadros, S., Manich, A. M., *et al.*; Reduction of the formaldehyde content in leathers treated with formaldehyde resins by means of plant polyphenols. *J. Cleaner Prod.* **148**, 518-526, 2017.
2. Wolf, G., Hoffer, S.; Formaldehyde in leather: a survey. *JALCA* **97**, 456-460, 2002.
3. Ghafari, R., Doosthosseini, K., Abdulkhani, A., *et al.*; Replacing formaldehyde by furfural in urea formaldehyde resin: effect on formaldehyde emission and physical–mechanical properties of particleboards. *Eur. J. Wood Prod.* **74**, 609-616, 2016.
4. International Agency for Research on Cancer; Chemical agents and related occupations, Volume 100 F, a review of human carcinogens. International Agency for Research on Cancer, pp. 401-436, 2012.
5. Kelly, F. J.; WHO Guidelines for Indoor Air Quality: Selected pollutants. 2010.
6. UK REACH.; REACH - Substances of Very High Concern. UK REACH Competent Authority Information Leaflet Number 12. 2009.
7. GB20400-2006, Leather and fur. Limit of harmful matter, 2006.
8. OEKO-TEX® Standard 100. https://www.oeko-tex.com/en/business/business_downloads/business_downloads.xhtml (Accessed 3 January 2019).
9. Dixit, S., Yadav, A., Dwivedi, P. D., *et al.*; Toxic hazards of leather industry and technologies to combat threat: a review. *J. Cleaner Prod.* **87**, 39-49, 2015.
10. Bayramoglu, E. E., Onem, E., Yorgancioglu, A., *et al.*; Investigation of the effects of various waste extracts on free formaldehyde in leather. *Tekst Ve Konfeksiyon*. **21**, 410-414, 2011.
11. ISO 17226-1-2018, Leather. Chemical determination of formaldehyde content. Pt. 1: method using high performance liquid chromatography, 2018.
12. Meyndt, R., Germann, H. P.; "Formaldehyde-free leather" - a realistic objective? Proceedings of the 28th IULTCS Congress. Florence of Italy. 2005.
13. ISO 27587-2009, Leather. Chemical tests. Determination of the free formaldehyde in process auxiliaries, 2009.

14. Douglas, C. M.; Three-Level and Mixed-Level Factorial Design and Fractional Factorial Design in Design and Analysis of Experiments, 7th ed., John Wiley & Sons Inc, pp. 66-68, 2008.
15. Ma, H., Huang, X., Zhang, D.; Determination of Free-formaldehyde in Aqueous Solution. *China Leather* **37**, 41-42, 2008.
16. Cama-Moncunill, X., Markiewicz-Keszycka, M., Dixit, Y., *et al.*; Feasibility of laser-induced breakdown spectroscopy (LIBS) as an at-line validation tool for calcium determination in infant formula. *Food Control* **78**, 304-310, 2017
17. ISO 5725-1-1994, Accuracy (trueness and precision) of measurement method and results. Pt. 1: general principles and definitions, 1994.
18. Xie, H., Sun, Q., Liao, X., *et al.*; Melamine Glyoxal resin as a retanning agent-preparation and application. *J. Soc. Leather Technol. Chem.* **98**, 17-22, 2014.