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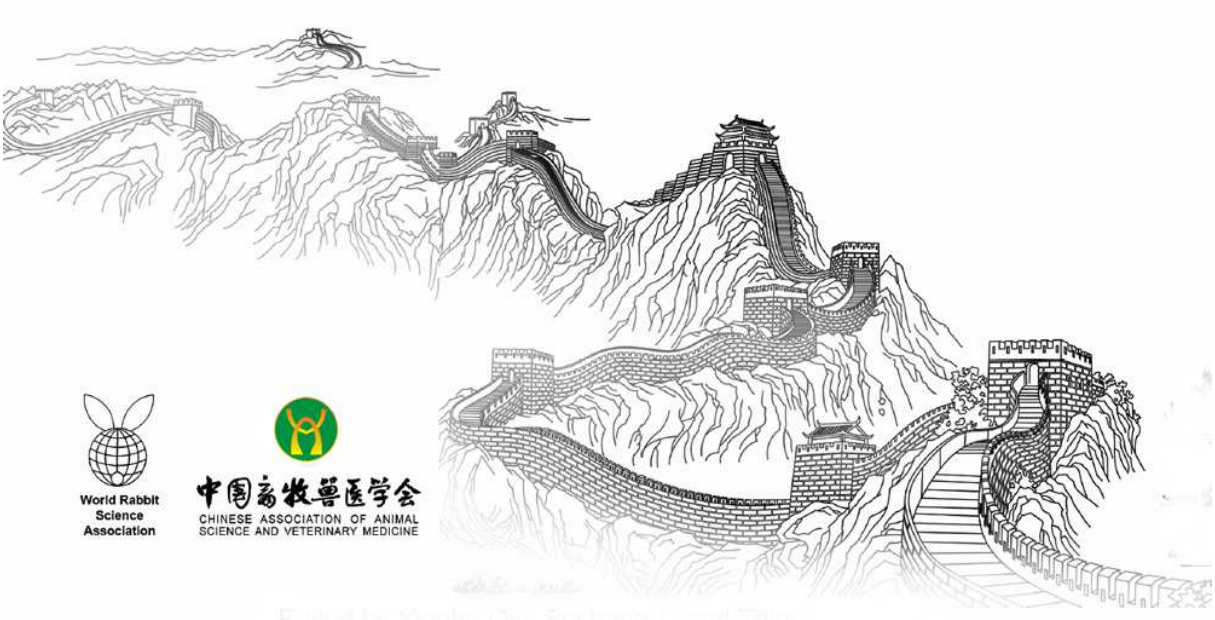

DETERMINATION OF FORMALDEHYDE AND GLUTARALDEHYDE IN RABBIT FUR BY HPLC

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ABSTRACT

A method for simultaneous determination of formaldehyde and glutaraldehyde by HPLC in rabbit fur was developed. The results show that the linear range of formaldehyde was between 0.1 μg/mL-50 μg/mL and glutaraldehyde was between 10 μg/mL-110 μg/mL, relative standard deviation (n=8) of formaldehyde was 4.84% and glutaraldehyde was 1.41%, and the average recovery rate was at the range of 92.2%-104.6%. The method is fast and accurate with good reproducibility and precision which meets the need for testing formaldehyde and glutaraldehyde simultaneously in rabbit fur.

Key words：HPLC；Formaldehyde；Glutaraldehyde；Determination；Rabbit Fur

INTRODUCTION

Formaldehyde (HCHO) and glutaraldehyde ($C_5H_8O_2$) have been widely used as raw materials in the chemical industry. Formaldehyde is a tanning agent in rabbit fur processing, which produces white rabbit fur with good qualify. But it is toxic volatile substances (Yan，2004; Jin, 2011), it damages the health of operators. And the formaldehyde in fur will release all the time which is harmful to the health of the users. So the determination of formaldehyde and glutaraldehyde extracted from fur is very important. High-performance liquid chromatography（HPLC） is widely used in separation and determination of various kind of mixture substance (Hu *et al.*, 2009; Jian *et al.*, 2013).
In this research, the determination of formaldehyde and glutaraldehyde content with HPLC was studied and rabbit fur tanned with aliphatic aldehyde tanning agent, the formaldehyde tanning rabbit fur and the modified-glutaraldehyde tanning rabbit fur samples were detected. The purpose of this study is to provide an efficient and accurate measurement method for the formaldehyde and glutaraldehyde content detection in fur products and provide reliable test data for the development, quality inspection and control of eco-leather and fur product.

MATERIAL and METHODS

Apparatus and materials

The HPLC was equipped with a variable wavelength detector and a 5 μm ZORBAX Eclipse Plus C18 column. Mobile phase: acetonitrile/water (V/V) =75/25. The separation of hydrazone was carried out at a flow-rate of 1mL/min. The effluent was monitored with a spectrophotometer at a wavelength of 350 nm (Wang *et al.*, 2011). 20μL of the methanol solution were injected into the HPLC when the column temperature under 25℃.
Formaldehyde (AR: Analytical reagent), acetonitrile (Guaranteed reagent), glutaraldehyde (AR) and concentrated phosphoric acid (AR) were obtained from ChengDu KeLong Chemical (Sichuan,China).

DNP-hydrazine (AR) was purchased from Tianjin Kermel Chemical Reagent Co. Quimitan FB is a kind of aliphatic aldehyde tanning agents which was purchased from QUIMIPLEL Leather Chemicals Co.

Methods

Accurately weight with Shredded rabbit fur sample 2g, placed in 250mL conical flask, stopper tightly after 50mL extraction solution (potassium dihydrogen phosphate solution) was added at 40℃, gently shock in the water bath pot shock for 60 min, then filtration to 100mL conical flask immediately, stopper tightly and natural cooling. 5mL above extract solution was added to 10mL volumetric flask, then 4mL of acetonitrile and 0.5mL of purified DNPH was added, dilute with high purity water and mix, derived 60min at room temperature, filtered with 0.22μm filter membrane polyamide, and then chromatographic analysis.

Formaldehyde and glutaraldehyde stock solution were diluted 500-fold, 1, 2, 3, 4, 5mL solution was transferred to a 10mL volumetric flask, then take the same measure as above, chromatographic analysis. The concentration standard curve is obtained.

RESULTS AND DISCUSSION

Qualitative analysis of HPLC peak and Optimization of derivative

5mL potassium dihydrogen phosphate solution, standard solution of formaldehyde and glutaraldehyde was added in 10mL volumetric flask separately, then handled as the samples above, the mixture of potassium dihydrogen phosphate with acetonitrile as the blank group, chromatographic analysis is as follows: the appearance time of derivative agent elution peak was about 3.1min; formaldehyde-DNPH eluting peaks appears for about 3.9min; the glutaraldehyde-DNPH appears a small peak at 7.44 min while it also appears a large peak at 8.3 min. The content of glutaraldehyde was calculated by the later peak.

5mL of 48.76 μg/mL formaldehyde standard solution was placed into 10mL volumetric flask.4mL acetonitrile was added, then followed by 0.1mL, 0.2mL, 0.3mL, 0.4mL, 0.5mL, 0.6mL, 0.7mL, 0.8mL DNPH was added, then take the same way as samples. To ensure the accuracy of test results, using 0.5mL as the amount of the derivatives in this experiment.

Precision experiment

1mL of 48.76μg/mL formaldehyde standard solution and 3mL of 57.04μg/mL glutaraldehyde standard solution was added in a 10ml volumetric flask separately. Then handled as samples above with 8 repeats (Table 1). Table 1 shows that, under the experimental conditions, precision of the method were less than 5% and with good reproducibility.

Table 1 The result of precision experiment of formaldehyde[a] and glutaraldehyde[b] standard solution by HPLC

Test times	1	2	3	4	5	6	7	8	RSD
Peak area（mAU•S）[a]	1819.5	1850.2	1875.4	1867.2	1929.1	1971.6	2017.2	2092.1	4.84%
Peak area（mAU•S）[b]	226.1	227.3	226.3	222.7	228	224.9	225.7	233.7	1.41%

The linear range of formaldehyde and glutaraldehyde by HPLC

Formaldehyde stock solution was diluted 50-fold and 500-fold, glutaraldehyde stock solution was diluted 500-fold and 5000-fold, taken 1, 2, 3, 4,5 mL diluted solution and transferred to a 10mL volumetric flask, then handled as the samples above.

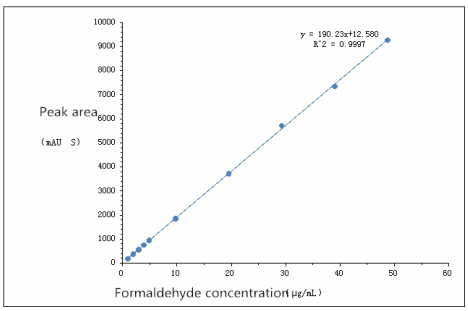

Fig.1 Relation between the formaldehyde standard solution and peak area

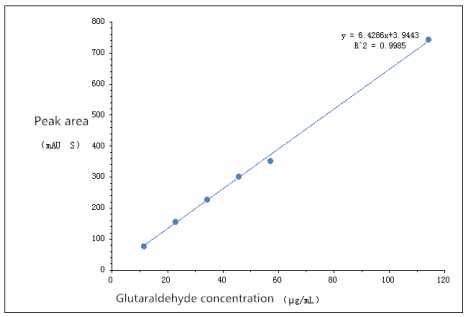

Fig.2 Relation between the glutaraldehyde standard solution and peak area

Results from figures 1 and 2 above, the detection of formaldehyde with a good linearity by HPLC in the concentration range from 0.974μg/mL to 48.76μg/mL. The detection of glutaraldehyde with a good linearity in the concentration range from 11.41μg/mL to 114.08μg/mL.

Sample test of rabbit fur

Take 5mL of extract solution of rabbit fur tanned with FB, formaldehyde and Modified-glutaraldehyde to 10mL volumetric flask, then handled as the Method mentioned above. The formaldehdyde and Glutaraldehyde content determined are showed in Table 2.

Table 2: The determination results of rabbit fur samples by HPLC

Rabbit fur sample	**Sample quality（g）**	**formaldehyde content（mg/kg）**	**Glutaraldehyde# content（mg/kg）**
Tanned with FB	2.0257	145.9	0
Tanned with Formaldehyde	2.0514	693.3	0
Tanned with Modified-glutaraldehyde	2.325	105.5	0

#The glutaraldehyde was not detected in the sample, and the flocculent precipitate did not appear at derivative process.

Recovery rate

Table 3 shows the results of recovery test. As we can see from Table 3 , The detection recoveries were in the range of 97.5% to 102.8% and with high degree of accuracy.

Table 3: Recovery rate of formaldehyde solutions

Rabbit fur sample	Peak area of sample（mAU•S）	Peak area of sample with added standard solution（mAU•S）	Recovery rate
Tanned with FB	594.1	1173.8	97.5%
Tanned with Formaldehyde	2787	5653.9	102.8%
Tanned with Modified-glutaraldehyde	498.3	987.3	98.1%

CONCLUSION

It was established a method to simultaneous determination of formaldehyde and glutaraldehyde content by HPLC in this article.

Under condition of experience, the precision of detection of formaldehyde was 4.84%, the correlation coefficient of standard curve in the concentration range of 0.1 μg/mL to 50 μg/mL was 0.9997. Precision of detection of glutaraldehyde was 1.41%, the correlation coefficient of standard curve in the concentration range of 10 μg/mL to 110 μg/mL was 0.9985. This method has good precision, high linearity of standard curve. The detection recoveries were in the range of 97.5% to 102.8% and with high degree of accuracy.

In this study, the formaldehyde and glutaraldehyde content of the FB, formaldehyde tanning and modified-glutaraldehyde tanning rabbit fur was detected. Result showed that the formaldehyde content is 146mg/kg, 685mg/kg and 110mg/kg respectively, the glutaraldehyde content of all samples is 0 mg/kg.

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REFERENCES

Hu Y., Zhang X., *et al.* 2009. Research progress and detection methods of formaldehyde.*J.Leather science and Engineering, 19,33-35.*

Jiang H., Zhang X., *et al.* 2013. Online analysis of formaldehyde in leather wastewater by reverse flow injection method. *J.Leather science and Engineering,23,68-71.*

Jin M. 2011. Occupation hazards and protective measures of glutaraldehyde for nurses. *J.Medical Theory and Practice, 24, 2895-2896.*

Wang C., Gong Y., *et al.* 2011.Determination of formaldehyde in leather by pre-column derivatization and high performance liquid chromatography.*J.Leather science and Engineering,21,47-52.*

Yan J. 2004. Formaldehyde and its harm to human health. *J.Chemical World, 45,558-559.*

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