Determination of Fatty Spew on Leather by GC-MS

by

Yanan Wang, Xuepin Liao, Qiang He and Bi Shi*

National Engineering Laboratory for Clean Technology of Leather Manufacture,

Sichuan University, Chengdu 610065, P. R. China

Abstract

The composition of fatty spew on leather was determined by gas chromatography-mass spectrometry (GC-MS). Meanwhile, the volatile substances in the fogging test of leather were identified by GC-MS. With the combination of all the data obtained, it was found that the predominant components of fatty spew were palmitic acid methyl ester, oleic acid methyl ester and stearic acid methyl ester, and their relative content ratio is approximately 8: 1: 1. An interesting phenomenon was that no fatty acids are detected in fatty spew although they are commonly regarded as the origin of this defect. These facts strongly suggest that the fatty acid methyl esters existing in fatliquors are the main origin of fatty spew defect in leather, and also one of the probable contributions to fogging.

Resumen

La composición de la exudación de grasa en el cuero fue determinada por cromatografía de gases y espectrometría de masas (GC-MS). Mientras tanto, las sustancias volátiles en la prueba de empañamiento (Fogging) del cuero fueron identificados por GC-MS. Con la combinación de todos los datos obtenidos, se comprobó que los componentes predominantes de la exudación grasa fueron el éster metílico del ácido palmítico, éster metílico del ácido oleico y el éster metílico de ácido esteárico, y su relación de contenido relativo es aproximadamente 8: 1: 1. Un fenómeno interesante es que no se detectaron ácidos grasos en la exudación grasa a pesar de que comúnmente se los considera como el origen de este defecto. Estos hechos sugieren que los metil-ésteres de ácidos grasos que existen en los engrases son el principal origen del defecto en la exudación grasa en el cuero, y también una de las probables contribuciones para el empañamiento (Fogging).

Introduction

The fatty spew that presents as white greasy coating or irregular fatty patches on leather surface is one of the most frequent defects of finished leathers. Once it occurs, the appearance and feel of leather will be seriously influenced. The free fatty acids existing in leather are commonly considered as the origin of fatty spew, because they poorly bind to leather fibers, and tend to migrate to leather surface and then crystallize there.[1] The natural fats remained in leather due to inadequate degreasing or introduced by fatliquoring may be hydrolyzed into fatty acids by microbial action under the storage condition of warmth and dampness.[1,2] Also fatty acids are possibly included in many kinds of fatliquoring agents. Therefore, the close relationship between the formation of fatty spew and the use of fatliquors should be concerned. Meanwhile, the composition of fatliquors is one of the most important factors that affect the fogging characteristics of finished leather. Some compounds in fatliquors that weakly bind to leather, such as free fatty alcohols, fatty acids, fatty acid esters and fatty amines, are likely to volatilize from leather and therefore, cause fogging effect.[3] This process is nearly the same as the formation of fatty spew. It is speculated that the fatty spew could be prevented by using specialized low-fogging fatliquors that have good fixing capacity with leather.[4]

Until now, the knowledge about the origin of fatty spew is usually obtained from experience rather than experimental evidence, and there is little literature concerning the identification of the composition of fatty spew by using analytical instruments. Gas chromatographic analysis of fatty spew was first reported by Tancous in 1974,[5] and then developed by Tomaselli et al in 2003.[6] They deduced from the chromatograms that some free fatty acids and glycerides should be the primary constituents of the fatty spew. However, the conclusion is not quite convinced due to the limitation of gas chromatography in qualitative analysis. Recently, Luo et al reported a new determination method of free fatty acids in leather.[7] In their study, the fatty acids in leather were extracted by dichloromethane and then methylesterified before gas chromatography-mass spectrometry (GC-MS) analysis. It was found that the leather samples exhibiting fatty spew contained higher contents of palmitic acid and stearic acid than the

*Corresponding author e-mail: sibitannin@vip.163.com

Manuscript received October 11, 2010, accepted for publication January 3, 2011

samples without fatty spew, which implies that these two compounds may be the origin of fatty spew.

GC-MS is a competent method to separate and identify the constituents of a complex mixture. In this study, the fatty spew was collected from leather surface and determined by GC-MS directly. In addition, the volatile ingredients derived from the fogging test were analyzed by GC-MS as well. The combination of the fogging test and GC-MS analysis may provide a better approach to understand the origin of fatty spew and to formulate the strategy of preventing leather from this kind of defect.

EXPERIMENTAL

Materials and general methods

The leather samples were cattle hide upholstery leathers supplied by a tannery in Zhejiang Province, China. Sample 1 presented serious fatty spew over the leather, while sample 2 had no spew on the grain surface.

The fogging characteristics of leather samples were determined by using HAAKE P2-FOG fogging tester (Thermo Fisher, Germany). The qualitative analysis of fatty spew and fogging precipitate was performed using a Trace gas chromatograph interfaced to a DSQ II quadrupole mass spectrometer (Thermo Fisher, USA).

Analysis of fatty spew composition

A piece of leather (3 cm×3 cm) was taken from leather sample 1. The fatty spew on the grain surface of the leather piece was lightly rubbed off by a piece of absorbent cotton that had been washed and soaked in anhydrous diethyl ether (analytical grade). Then the absorbent cotton was repeatedly washed by diethyl ether. The eluant containing fatty spew was collected and passed through a 0.45 μm membrane filter. Then the filtrate was qualitatively determined by GC-MS.

The GC-MS analysis was performed under following conditions. The GC instrument was equipped with a TR-5MS capillary column (30 m×0.32 mm I.D., 0.25 μm film thickness, Thermo Fisher). The oven temperature was programmed from 40°C (held for 1 min) to 250°C at a rate of 10°C /min, and then held at 250°C for 5 min. The carrier gas was helium (purity 99.999%) at constant flow of 1.0 ml/min. The inlet temperature was kept at 260°C and split mode (split ratio 20: 1) was used for injection. The mass spectrometer was operated in electron impact ionization (EI) mode at 70eV. Both the ion source temperature and the transfer line temperature were 250°C. The scan mode was the full scan in mass range from 40 to 400 *m/z*.

Analysis of fogging precipitate composition

The fogging behaviour of the two leather samples was determined according to the method B (gravimetric method) of IUP 46 Standard.[8] The procedure of this method can be briefly summarized as follows. A dried leather piece was heated in a sealed glass beaker, so that the volatile substances evaporated from the test piece and then condensed on a cooled aluminium foil that was placed on top of the beaker. After a period of 16h the aluminium foil was moved into a desiccator and stilled for 4h. Then the fogging precipitate condensed on the aluminium foil was rinsed out by anhydrous diethyl ether. The eluant was collected for GC-MS analysis.

The GC oven temperature was programmed from 150°C (held for 3 min) to 230°C at a rate of 10°C /min, and then held at 230°C for 5 min. The inlet temperature was 250°C. The other GC-MS analysis conditions were the same as for fatty spew analysis.

RESULTS AND DISCUSSION

The composition of fatty spew

Figure 1(a) is the total ion current (TIC) chromatogram of the fatty spew from leather sample 1, determined by GC-MS. The identification of the compounds in the TIC chromatogram was conducted by comparison of the mass spectra obtained by GC-MS with those in standard library data (NIST 05). Fatty acid methyl esters were found to be the main constituents of the fatty spew from the searching results. However, the background of the TIC chromatogram is relatively high due to the complexity of fatty spew, which makes it difficult to separate and quantify the co-eluting components. In this situation, extraction of the characteristic ions for the target compound could be efficient to solve the problem. Based on the mechanisms of ion fragmentation in the interpretation of mass spectra,[9,10] the methyl esters which can form a 6-membered ring transition state usually undergo a cyclic fragmentation called McLafferty rearrangement, as shown in Figure 2. This rearrangement involves a transfer of a γ-hydrogen atom to the carbonyl oxygen atom and a β-cleavage reaction, leading to the formation of a characteristic peak at *m/z* 74. Figure 1(b) displays the mass chromatogram of the ion *m/z* 74 of the fatty spew sample. It is clear that the background is subtracted and a series of intense GC peaks are revealed after the extraction of the characteristic ion (*m/z* 74). The identification of the peaks and the calculation of their relative contents by peak area normalization were completed on the basis of Figure 1(b), and the results are summarized in Table I. The fatty spew on leather sample 1 is mainly composed of palmitic acid methyl ester, oleic acid methyl ester, stearic acid methyl ester and their isomers. The relative contents of these three esters are 85.4%, 7.7% and 6.8%, respectively. These results are different from the previous conclusions that fatty spew mainly results from free fatty acids.[5-7] To confirm our results, more investigations will be carried out in the following section.

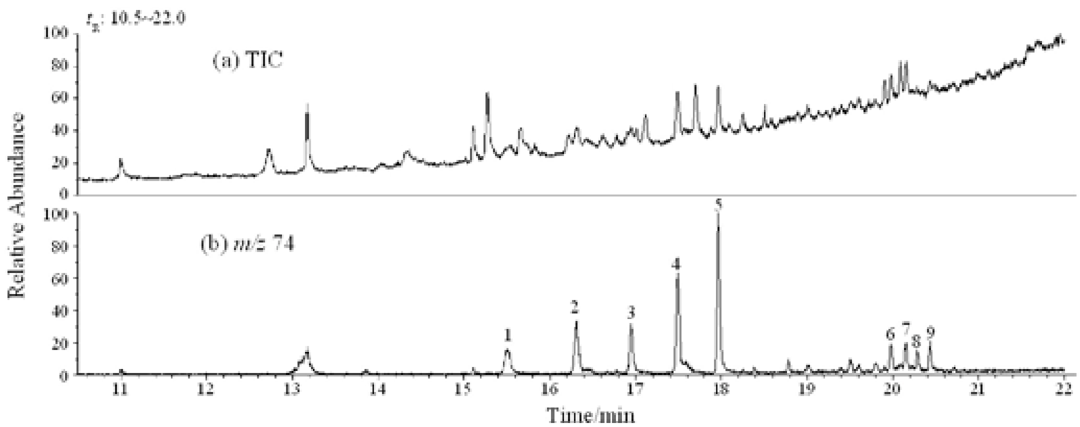

Figure 1. The chromatograms of fatty spew: (a) total ion current (TIC); (b) ion current of *m/z* 74.

The composition of fogging precipitate

The fogging characteristics of the two leather samples were determined. The difference between the leather samples was that fatty spew only occurred on sample 1. It was found that the fatty spew on sample 1 disappeared after fogging test, and did not recurred during the next two months. This phenomenon suggests that the compounds that form fatty spew in leather sample 1 completely volatilized under the test conditions. The volatile substances were collected and analysed by GC-MS so that more information about the composition of fatty spew can be obtained.

Figure 3(a) and 3(b) are the TIC chromatograms of the fogging precipitates derived from sample 1 and sample 2, respectively. Some volatile aliphatic and aromatic hydrocarbons are observed both in Figure 3(a) and 3(b). But some peaks only exist in Figure 3(a) (labelled as peak 1, 2 and 3), and they are identified to be palmitic acid methyl ester, oleic acid methyl ester and stearic acid methyl ester by comparison of their mass spectra and retention times to those of standards. That is to say, these three methyl esters are only present in the fogging precipitate of the leather with fatty spew. These esters can also be distinctly observed from the mass chromatogram of m/z 74, as shown in Figure 3(c). Compared with Figure 1(b), the isomers of the esters are not separated in this chromatogram due to the higher initial temperature of GC oven.[11] The relative contents of the three esters in the volatile substances are listed in Table II. The content ratio of the three esters is approximately 8: 1: 1, which is consistent with the composition of fatty spew shown in Table I. These results further prove that fatty acid methyl esters are the predominant constituents of fatty spew on leather sample 1.

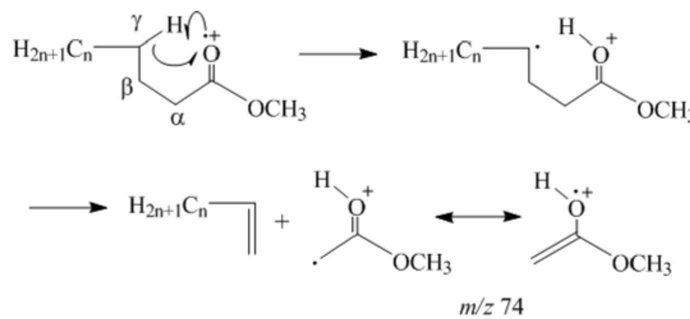

Figure 2. The McLafferty rearrangement reaction of fatty acid methyl esters.

TABLE I
The Identified Compounds in Fatty Spew

Peak No.	Retention time/min	Formula	Compound	Content/%*
1, 2, 3, 4, 5	15.50, 16.31, 16.95, 17.49, 17.96	$C_{17}H_{34}O_2$	palmitic acid methyl ester and its isomers	85.4
6, 7	19.98, 20.15	$C_{19}H_{36}O_2$	oleic acid methyl ester and its isomers	7.7
8, 9	20.28, 20.44	$C_{19}H_{38}O_2$	stearic acid methyl ester and its isomers	6.8

[*] The relative contents were calculated by peak area normalization

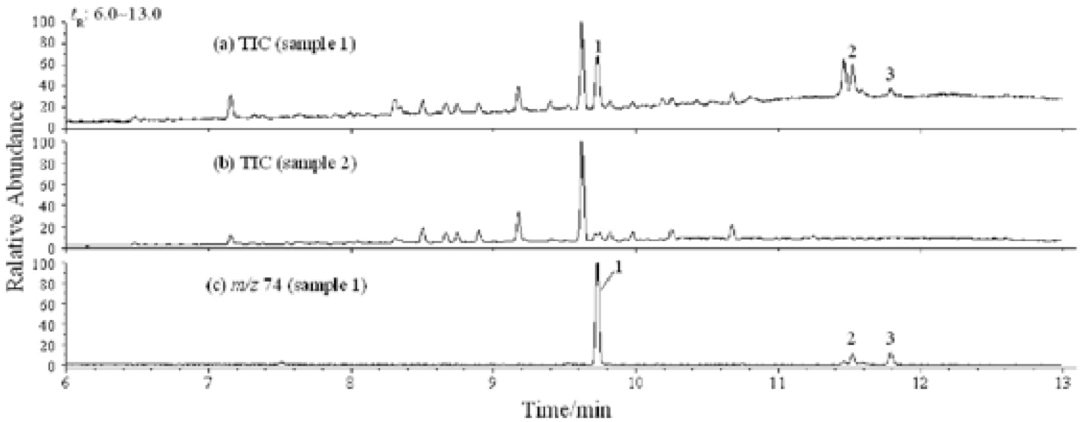

Figure 3. The chromatograms of the fogging precipitates: (a) total ion current (TIC) of sample 1; (b) total ion current (TIC) of sample 2; (c) ion current of *m/z* 74 of sample 1.

TABLE II
The Identified Compounds of the Volatile Ingredients in Leather Sample 1

Peak No.	Retention time/min	Formula	Compound	Content/%*
1	9.73	$C_{17}H_{34}O_2$	palmitic acid methyl ester	78.1
2	11.53	$C_{19}H_{36}O_2$	oleic acid methyl ester	10.3
3	11.79	$C_{19}H_{38}O_2$	stearic acid methyl ester	11.6

* The relative contents were calculated by peak area normalization

Effect of fatliquors on occurrence of fatty spew

All the results obtained in our researches indicate that it was fatty acid methyl ester that leads to the formation of fatty spew on leather surface. Fatty acids were not detected in fatty spew although they are commonly regarded as the origin of this defect. The composition of fatty spew may depend on the character of leathers being determined, particularly the degreasing conditions and the fatliquors used in leather processing. But anyway, our results could be reasonable in consideration of the structures of fatliquors being commonly used in tanneries nowadays. As we know, most of fatliquors are produced from natural fats, and alcoholysis or transesterification reaction of natural fats with methanol is often carried out in order to improve fatliquoring performance of products. As a result, the products contain a large amount of free fatty acid methyl esters.[12] When they are used for fatliquoring, the free fatty acid methyl esters will be distributed in leather. It can be speculated that the fixation of free fatty acid methyl esters with leather would be weaker than fatty acids and other components because their reactive groups, i.e. carboxyls, are esterified. Therefore, the esters are likely to migrate to the leather surface and crystallize into fatty spew during the storage.

CONCLUSIONS

Fatty acid methyl esters existing in leather, such as palmitic acid methyl ester, oleic acid methyl ester and stearic acid methyl ester, are the main components that cause fatty spew defect in leather. These synthetic compounds would be introduced into leather when the fatliquors containing free fatty acid methyl esters are used in leather processing. The composition of fatty spew can be identified quickly and accurately by GC-MS. Furthermore, the substances that form fatty spew will completely volatilize from leather in fogging test. Therefore, the possibility of fatty spew occurrence on leather can be evaluated through identifying the components of the volatile substances from fogging test by GC-MS. Similarly, it may be possible to predict the composition of the volatile substances found in fogging by identifying the components of the fatty spew. The long-range strategy to eradicate leather spew defect, is for suppliers to label their fatliquors "Contains synthetic components known to cause fatty spew".

ACKNOWLEDGEMENT

This project is financially supported by the National Technologies R&D Program (2006BAC02A09).

REFERENCES

1. John, G.; Possible defects in leather production, Druck Partner Rübelmann GmbH, Hemsbach, 1996.
2. O'Flaherty, F., Roddy, W. T. and Lollar, R. M.; The chemistry and technology of leather (Volume 4), Reinhold Publishing Corporation, New York, 1965.
3. Götz, O.; Factors determining the occurrence of fogging behavior of automotive leathers. *J. Soc. Leather Technol. Chem.* **83**, 149-153, 1999.
4. Zhu, C. F. and Yu, G. P.; Mechanism and handle technology of leather spew. *China Leather* (Chinese) **37**, 3-4, 2008.
5. Tancous, J. J.; A study of fat spew by gas chromatography. *JALCA* **69**, 66-84, 1974.
6. Tomaselli, M., Naviglio, B., Naviglio, D., et al.; Fats and fatty spues: a gaschromatographic characterization. XXVII IULTCS Congress, Cancun, 2003.
7. Luo, X. M., Ma, H. W., Li, P. N., *et al*.; Study on the determination methods of free fatty acids in Leather. XXX IULTCS Congress, Beijing, 2009.
8. IUP 46, Measurement of fogging characteristics. *J. Soc. Leather Technol. Chem.* **86**, 73-76, 2002.
9. McLafferty, F. W.; Interpretation of mass spectra, University Science Books, Mill Valley, 1980.
10. Field, L. D., Sternhell, S. and Kalman, J. R.; Organic structures from spectra, John Wiley and Sons Ltd, West Sussex, 2008.
11. Hübschmann, H. J.; Handbook of GC/MS: fundamentals and applications, Wiley-VCH Verlag Gmbh & Co. KGaA, Weinheim, 2009.
12. Lu, L.; Alcoholysis reaction in fatliquor synthesis. *Leather Chemicals* (Chinese) **18**, 35-37, 2001.