The Smell of Leather

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Abstract: One of leather's important characteristic is its smell. In contrast to synthetics the leather smell is desired and regarded as an attribute of authenticity by customers in many countries. For research works 5 different leathers from different application areas were chosen. Depending on manufacturing technology the leathers showed different nuances of leather smell. Presentation gives results from analysis of leathers by GC-O, AEVA, GC-MS and SIVA for identifying and quantifying substances accountable for certain leather smells. Furthermore, it points out from which stages of leather manufacturing the leather smell originates and if it can be influenced. Alternative methods for identification and quantification of substances relevant to smell are discussed regarding their informational value.
Key words: leather smell; sources; identification; alternative methods

1 Introduction

The typical smell of leather still is an important characteristic influencing purchase decision. Many customers consider the leather smell to be proof of authenticity. Whereas most other materials are expected to be free of smell, with leather a certain smell is desired explicitly.

Up to now it was known, that leather smell can be influenced by selection of fat liquors and retanning agents[1]. Furthermore some single substances responsible for off-odours are known [2]. Based on long-time experiences with emissions tests and odour assessment of leather in FILK it was assumed that a mix of substances (i.e. aldehydes, ketones, phenolic compounds) is causing the typical leather smell. Furthermore it can be noticed that the standard emission test methods are not sufficient for clarification of sources of leather smell [3].

Necessity to clarify the intense odorants in leather and their sources derive from the demands for influencing the leather smell systematically and reproducible during the process of manufacturing.

In a mutual research project of FILK and the German Research Center for Food Chemistry substances accountable for leather smell were identified. With the knowledge of structure and characteristics of these components the development of simplified rapid methods for routine measurements was attempted.

The following information refers solely to substances accountable for the regular pleasant leather smell. The identification of off-odours was not subject to research works.

2 Experimental

2.1 Selection of Leathers

For research works the following materials were chosen:

- Automotive leather (AL) – chrome-tanned
- Upholstery leather (PL) - chrome-tanned

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- Shoe upper leather (SL) - chrome-tanned
- Sole leather (BL) – purely vegetable-tanned
- LEFA – Leather fibre board (manufactures from leather fibres and latex)

A substantial number of persons dealing with leather on a daily base were involved in choosing the materials. Great attention was paid to choosing leathers featuring a characteristic, pleasant smell typical for their groups. All leathers were investigated in crust-stage which is without any finish.

2.2 Methods for Identification of Compounds Relevant to Odour

For identification of intense odorants a classical approach of aroma analysis was applied. The method was described in detail at the conference „Emissions and odours of materials“ 2008 in Brussels [4]. With this the significant steps are:

- AEDA (aroma extract dilution analysis)
  Solvent extraction, odour comparison, isolation of volatile fractions, concentration, GCO, dilution step by step
- Identification of intense odorants
  Comparison of retention index, odour quality, and mass spectrum of odorant and reference compounds
- SIDA – Stable isotope dilution analysis
  Quantification with isotopic labelled standards as an internal standard using GC/MS
- Determination of odour activity value = ratio of concentration and odour threshold
  Complies with the substance’s relative portion in leather odour, determination of odour thresholds in gelatine
- Simulation of odour
  Reconstitution of odour – comparison with original

3 Results and discussion

3.1 Identification of Intense Odorants in Leather

First steps in identification of compounds relevant to odour (AEDA) confirmed assumptions that several substances are involved in the formation of leather smell. Furthermore, it turned out that a mayor part of the listed compounds was found in nearly every leather analysed in the course or research. Altogether, clearly more than 70 different compounds possibly contributing to leather smell were identified. The following list names substances with highest intensities and Flavour Dilution Factors, respectively. Though this list gives only a first reference to possible sources of leather smell as actual portions and odour thresholds of the compounds are not accounted for yet:

- gamma-nonalactone
- vanillin
- 4-allyl-2-methoxyphenol (eugenol)
- phenylacetic acid
- 2,6-dichloromethylphenol
- 4-chloro-3-methylphenol (CMK)
- 5-methyl-2-methoxyphenol
- 2-methoxyphenol
- benzothiazol
- 2,4,6-trichloroanisol
- 2-phenylphenol (OPP)
- (E,Z)-2,6-nonadienal

- (Z)-2-nonenal
- 2,4,6-tribromoanisol

3.2 Results Quantification and Aroma Values

For quantification a stable isotopic labelled standard of each identified odour-relevant substance was used. It became obvious that in almost every analysed material nearly the same substances are accountable for the smell. Differences occur solely in concentration and aroma values respectively. The following list contains the most important substances accountable for the typical leather smell:

- 4-chloro-3-methylphenol (CMK)
- (E)-2-nonenal
- hexanal
- benzothiazol
- (E,Z)-2,6-nonadienal
- (E,E)-2,4-decadienal
- octanal
- (E,E)-2,4-nonadienal
- (Z)-4-heptenal
- nonanal
- gamma-nonalactone, gamma-octalactone
- 4-ethyl-2-methoxyphenol, 5-methoxy-2-phenol (sole leather only)
- vanillin, phenol, 4-methylphenol
- 2-phenylphenol (OPP)
- 2,4,6-tribromoanisol, 2,4,6-trichloroanisol, 2-(methylthio-)benzothiazol (leather board only)

3.3 Sources of Intense Odorants

From analyses of auxiliaries used during the tanning process and leathers in different stages of manufacturing process following findings can be stated:

- Aldehydes and lactones can be related to fat liquors and their degradation products.
- Phenolic compounds result from vegetable tanning and retanning agents.
- Halogenated phenols, 2-phenylphenol and benzothiazole originate from preservative agents and their reaction products respectively.

3.4 Development of Rapid Test Methods

With the knowledge of structures and characteristics of intense odorants in leather rapid test methods on the base of emission-analytical techniques should be developed, thus enabling for a quick routine determination of these substances.

The following methods were applied:

- direct thermal desorption
- static headspace
- thermal extraction followed by thermal desorption

For detection a GC-system with parallel detection at MS as well as with sniffing-port were applied in each case.

It occurred that the amounts of emitting substances by static headspace are too low for parallel detection at MS and sniffing-port despite a temperature of 120 °C. Hence, low concentrated aroma substances could not be detected. The same applies for direct thermal desorption as the applicable sample quantity is too low. In addition, this method discriminates highly volatile substances. Moreover, the high water content of leather interferes with this method. Substantial amounts of compounds could be concentrated by thermal extraction only. A temperature of 50 °C showed to be sufficient for extraction.

Although higher temperatures could be applied it is not recommended due to thermal sensitivity of some of the analytes.

With external accumulation by thermal extraction and subsequent thermal desorption of the cumulated analyte of the used adsorbent a relatively high amount of substance reaches the column in GC. This amount is barely to manage with a common separating column. But not all searched odour-relevant substances are found in the chromatograms. On the one hand massive overlappings in some areas of the chromatograms occur due to the high amounts of substances. Thus some of the searched aldehydes lay beneath huge oil mounts and are difficult to trace even in SIM-mode. On the other hand detection of low-volatile analytes by external accumulation fails or is managed only with very low amounts in the chromatogram. With these difficulties proportion ratios of intense odorants attained by thermal extraction do not reflect real proportional composition of odour.

It became obvious that, despite the knowledge of the intense odorants in leather, it is not possible to reflect real proportion crucial for odour by emission-analytical methods.

4 Conclusions

The intense odorants in leather could be determined by means of aroma analysis techniques. The leather odour reflects a mixture of odour-active substances whereas variations of the diverse leather smells are caused by different concentration ratios of the substances. The sources of leather smell are mainly fat liquors, retanning agents and preservative agents.

Rapid test methods on the base of techniques of emission analysis proofed not appropriate for reflecting leather smell in a precise manner.

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