The Odor of Leather

by

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Abstract

Leather has a typical odor that varies depending on the type of leather. Whereas many other materials should preferably be odorless, a typical leather odor is desired. It is an important quality feature. So far the compounds causing the leather odor could not be clearly defined. For this research work, different leathers from different application areas were chosen. Depending on the manufacturing technology the leathers showed different nuances of leather odor. Published herein are the results from analysis of leathers by Gaschromatography-Odorimetry (GC-O), Aroma-extract-dilution analysis (AEDA), Gas chromatography-Mass-Spectrometry (GC-MS) and Stable-Isotope-Dilution-Analysis (SIDA) for identifying and quantifying substances accountable for certain leather odors. Furthermore, it points out from which stages of leather manufacturing the leather odor originates and if it can be influenced. Alternative methods for identification and quantification of substances relevant to odor are discussed regarding their significance.

Resumen

El cuero tiene un olor típico que varía en función del tipo de cuero. Mientras que muchos otros materiales preferentemente deberían ser inodoros, un típico olor a cuero es deseable. Es una característica importante de calidad. Hasta ahora, los compuestos que provocan el olor de cuero no pudo ser claramente definido. Para este trabajo de investigación, distintos cueros de diferentes áreas de aplicación fueron elegidos. Dependiendo de la tecnología de fabricación, los cueros mostraron diferentes matices de olor a cuero. Publicado en este documento se presentan los resultados del análisis de los cueros mediante Cromatografía de gases-Odorimetría (GC-O), Análisis de dilución de extracto de aroma (AEDA),Cromatografía de gases y Espectrografía de Masas (GC-MS) y Análisis de dilución de isótopos estables (SIDA) para identificar y cuantificar las sustancias responsables de ciertos olores de cuero. Por otra parte, señala a partir de qué etapas de fabricación del cuero se origina el olor y si pueden ser influenciados. Métodos alternativos para la identificación y cuantificación de sustancias relevantes para el olor se discuten con respecto a su significado.

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INTRODUCTION

The typical leather odor develops during production, which comprises a large number of process steps. So far, it is only known that the odor of leather can be influenced by selected fat liquors and re-tanning agents.[1] In some cases substances causing falsified odors could be identified.[2] Attempts to distinguish leathers with different odors using sensor systems were not successful.[3] A large number of volatile compounds not relevant for the odor have a stronger influence to the sensor signals than substances causing odor. It is not possible to determine the composition of the leather odor from results of emission tests.[3-5]

Therefore, the object of this present paper was to decode the characteristic leather odor in terms of quality and quantity. In addition, the influence of the individual production steps and additives on the leather odor was examined. For this purpose methods of food analytics for the identification of aroma substances were applied for the first time: Aroma-extraction-dilution analysis (AEDA)[6,7] aroma-dilution analysis (ADA), stable isotopes dilution analysis (SIDA).[8] All these methods are very time-consuming. For this reason, another effort was to develop a rapid gas chromatographic method based on emission analytics in order to determine the leather compounds relevant for the odor.

EXPERIMENTAL

Leather Selection

Leathers were chosen which showed a typical leather odor according to the evaluation of an experienced odor panel:

- Automotive leather (AL) – chrome-tanned
- Shoe upper leather (SL) – chrome-tanned
- Sole leather (VL) – purely vegetable-tanned

An upholstery leather and a leather fiber material (Lefa) were also examined.

Isolation of Volatile Substances

Solvent Extraction

The leather (1-10 g) is cut into small pieces (5 x 5 mm) and extracted with dichloromethane (50 ml) for 4 hours. After filtering out the leather pieces, they are extracted for another 1 hour. The odor of the extract is compared to the odor of the leather in terms of similarity. The volatile compounds of the unified extracts are isolated under high vacuum (5 mPa, 50°C) [7]. The distillate is concentrated by micro distillation[9] at a Vigreux column to about 0.1 ml.

Headspace Extraction

For headspace extraction the leather (1-10 g) is cut into small pieces (5 x 5 mm) and transferred to an iodine determination flask. This flask is closed with a septum and the culture is incubated for 1 hour at 20°C.

Aroma-extract-dilution Analysis (AEDA)

The solvent extracts containing dichloromethane (1:2, v/v) were gradually diluted, and all solutions were analyzed using gas chromatography with parallel odor detection port and flame ionization detector until no odor was perceivable. The FD (flavor dilution) factor of an aromatic substance was defined as being the highest dilution level at which the smell of the compound can still be perceived.[6]

Aroma-dilution-analysis (ADA)

Aliquots of the gas space (0.31 - 20 ml) of the headspace samples were taken with a gas-tight syringe and analyzed using gas chromatography with parallel odor detection port and flame ionization detector. The FD (flavor dilution) factor of an aromatic substance was defined as being the quotient of the highest injected volume and the lowest volume at which a compound can still be perceived.[10]

Identification of Key Odorous Substances

Capillary Gas Chromatography/Odorimetry (GC-O)

Separation of the odorous extracts was carried out with a GC type 5160 (Carlo Erba) with the capillary columns DB-5 and DB-FFAP (J & W Scientific). The eluents were split at the capillary end 1:1 (v/v) and transferred via two glass capillaries[11] to a flame ionization detector (FID) and a odor detection port (ODP).

For separating the headspace samples a GC type CP-9001 connected with a purge-and-trap-system TCT/PTI (Chrompack) with a capillary column RTX 5 (Amchro) was used. The eluents were split the same way and detected parallel ODP and FID. The volatile substances were cryo-focused at -110°C and thermally desorbed to the capillary column at 250°C.

Capillary Gas Chromatography/Mass Spectrometry (GC/MS)

For detection of the substances according to the GC separation a mass spectrometer MAT-95 S (Finnigen) with electron impact ionization (MS-EI) or a Saturn 2000 mass spectrometer (Varian) with chemical ionization (CI) was used.

Two-dimensional GC/MS (TDGC/MS)

TDGC/MS-analyses were performed with a moving column stream system (MCSS) according to reference.[12]

Identification and Structure Clarification

The aroma substances were identified by comparison of the retention indices at the capillary columns, the odor qualities and the mass spectrums with the reference compounds.

Quantification of Key Odorous Substances (SIDA)
Standards labelled with isotopes of the known quantities were added after solvent extraction and the volatile compounds were isolated. The extracts obtained were analyzed using GC/MS and two-dimensional GC/MC in CI mode. The ingredients were determined by intensity ratio of selected m/z ions of analyte and standard.

Sensory Examinations
Triangle Tests
For detecting significant differences of leather odors triangle tests according to Czerny et al[13] were performed by a trained sensory panel of ten persons and evaluated accordingly.[14]

Aroma Profile Analysis
The characteristic odor qualities and intensities were determined by a trained sensory panel of ten people. The intensities were assessed on a scale of 0 (imperceptible) to 3 (intensely perceptible). Calibration was performed by the sensory panel using corresponding reference solutions.

Determination of the Odor Threshold in Gelatin
A known quantity of a dissolved odorous substance was added to gelatin, which was deodorized in a Soxhlet-apparatus with Dichlormethane and homogenized under stirring in a flask. After evaporation of the solvent the concentration of the odorous substance in the gelatin was determined using the stable isotope dilution analysis. The gelatin blended with an odorous substance was gradually diluted and presented to the sensory panel until no odor was perceived.

Simulation of the Leather Odor
Defined quantities of odorous substances were dissolved and diluted with tap water until the concentrations of the odorous substances were identical with those in the leather samples. The solutions were mixed with sunflower oil, then an aroma profile analysis was performed by the sensory panel. In addition, the similarity of the odor with the leathers was assessed on a scale of 0 (no similarity) to 3 (identical), and the arithmetic average of the results was calculated.

Sample Preparation – Development of Rapid Tests
Headspace
A sample of 3 g was incubated at 120°C for 5 hours and an aliquot of the headspace was transferred to the GC column using a syringe injection system (Gerstel).

External Enrichment and Thermal Desorption of Volatile Compounds
A sample of 3 g was incubated in a glass-tube at different temperatures under nitrogen flow. The volatile compounds were adsorbed to Tenax® tubes. The Tenax® tubes were heated to 120°C in a thermal desorption system TDS5 (Gerstel) and the volatile compounds were transferred to the GC column (DB5) after cryo-focusing in a cryo-trap cooled with liquid nitrogen at – 150°C followed by thermal release at 280°C.

Capillary Gas Chromatography/Mass Spectrometry (GC/MS) Development of Rapid Tests
For separating the volatile compounds a gas chromatograph 5680 (Agilent) was used with a mass spectrometer (Agilent) with electron impact ionization. At the end of the capillary column the eluents were separated in a ratio of 1:4 (v/v) for parallel detection at the mass spectrometer (MS) and odor detection port (ODP).

RESULTS

Sensory Comparison of the Leathers Examined
Triangle tests were used for sensory examination of the leathers. It was found that the leather samples differed from each other to a high degree in terms of odor. The odor differences were described in more detail through aroma profile analyses. A trained sensory panel determined the following characteristic leather odor qualities: fatty, like cardboard, phenolic sweet, fecal - like horse stable, moldy-musty, rubber-like, ink-like - phenolic, plastic-like sweet and medically rubber-like. For a detailed characterization of the individual samples, the intensities of the odor qualities were subsequently assessed on a scale of 0 (imperceptible), 1 (slightly perceptible), 2 (clearly perceptible) to 3 (intensely perceptible) using reference aroma substances. Figure 1 shows the result of an aroma profile analysis of a sole leather (VL) sample. Phenolic sweet, cardboard-like and fecal - horse like odors were dominating. The intensity of the odor impressions were perceived in the range of only slightly up to clearly.

Figure 1-3 shows the comparing aroma profile analyses of sole leather with automotive leather and shoe upper leather. The ink-like phenolic and moldy-musty odor was much stronger perceived in automotive leather (AL) and shoe upper leather (SL), whereas particularly the phenolic sweet odor was less distinct. However, intensity of the plastic-like, rubber-like and medical odor in AL and SL were more significant than in VL. In addition, the fatty odor was perceived strongly in AL and SL, the cardboard-like odor was stronger in SL.

Identification of the Odorous Substances in Leather and Their Contribution to the Odor
For extracting the odorous substances from leather, different solvents were tested first. The dichloromethane extracts from leather reflected odors very well. They contained all important odorous substances. Other solvents, such as diethyl ether and n-pentane showed poorer results. For this reason dichloromethane was used for all extractions. The AEDA showed that the leather odor was composed of a large number of aromas. More than 70 odor-relevant substances were found in the aroma extracts of the leathers examined. Table 1 showed the flavor dilution factors of the detected odorous substances in the leather samples examined.

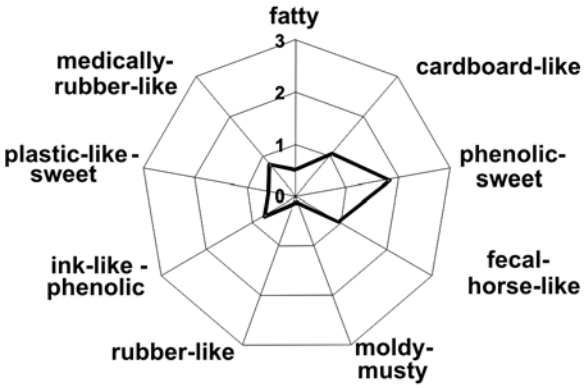

Figure 1. Aroma profile analysis of sole leather.

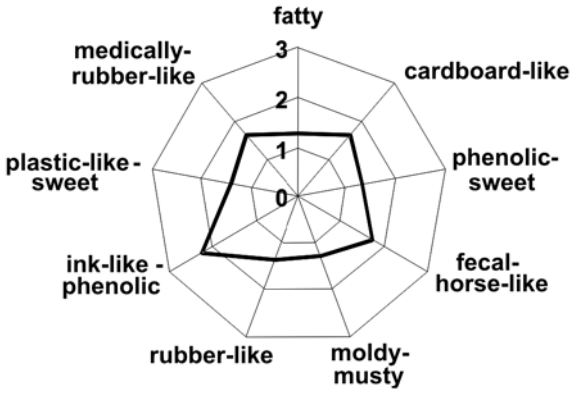

Figure 2. Aroma profile analysis of automotive leather.

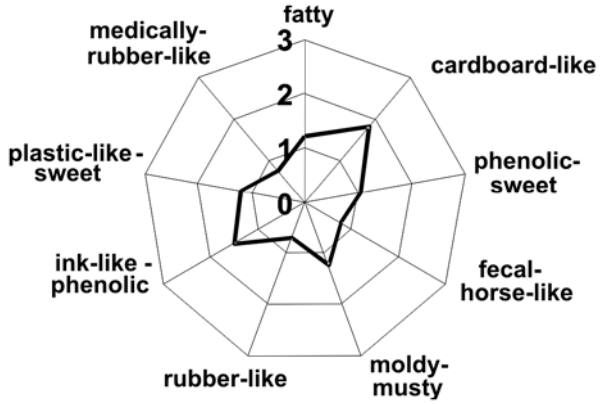

Figure 3. Aroma profile analysis shoe upper leather.

From the 79 detected odorous substances, 51 could be clearly identified. Odors of the leathers were individually composed of odor-relevant compounds. A range of odor-relevant substances (e. g. hexane) could be found in all leathers examined.

For the substances with the highest FD-factors and the substances for which great differences occurred between the leather types concentrations were determined using the SIDA method (table 2).

The concentration of odorous substances alone do not provide information about the contribution of the compound to an odor, as the odorous activities of odorous substances differ very strongly.[15] For this reason the aroma values (AV) of the odorous substances were calculated in another step. The aroma value is the quotient of concentration and odor threshold of a compound.[16] Thus, the relative contribution of any single odor-relevant component to the total odor can be assessed by comparison of the aroma values. The higher the aroma value the higher the contribution of the compound to the odor. Aroma values <1 indicate that there is no contribution to the odor.

The odor thresholds have to be determined in a matrix similar to the sample in order to simulate interactions between the odorous substance and the matrix as close and comparable as possible. The preparation of collagen or other leather materials for this purpose would be too expensive. For this reason bovine gelatin was used. The gelatin is not odorless. It was deodorized by extraction with dichloromethane and subsequent drying. After determination of the odor thresholds of these substances in gelatin, the aroma values were determined from these substances and their concentrations.

Table 3 shows a comparison of the aroma values of the key odorous substances of the leathers examined.

In sole leather (E)-2-nonenale (23) was calculated having the highest aroma value of 166. The aroma values of (E,Z)-2.6-nonadienale (25), 2-methoxyphenol (41), 4-ethyl-2-methoxyphenol (53), hexane (6), g-nonalactone (52), octanale (12), 4-methylphenol (58), (E,E)-2.4-decadienale (38) and 2-hydroxybenzaldehyde (30) in addition were in an AV range of 8 - 34 (tab. 3). The results allow the conclusion that (E)-2-nonenale, 2-methoxyphenol and 4-methylphenol are responsible for the characteristic odors (cardboard-like, phenolic-sweet or fecal - like horse stable, figure 1).

In AL also (E)-2-nonenale (23) was determined having the highest aroma value, followed by hexane (6), 4-chloro-3-methylphenol (76), (E,Z)-2.6-nonadienale (25), (E,E)-2.4-decadienale (38), (Z)-4-heptenale (11), (E,E)-2.4-nonadienale (33), g-nonalacton (52), octanale (12), 1-octen-3-on (13), nonanale (16) and 2-phenylphenol (79) in an AV range of 7 – 297.

In SL hexane (6) was determined having the highest AV of 452. In addition, (E)-2-nonenale (23), (E,E)-2.4-decadienale (38), octanale (12), 1-octen-3-on (13), (Z)-4-heptenale (11), (E,Z)-2.6-nonadienale (25), nonanale (16), (E,E)-2.4-nonadienale (33), 4-chloro-3-methylphenol (76), g-nonalacton (52) and benzothiazole (45) were calculated having aroma values between 9 and 143 (tab. 3).

The compounds 23, 33, 38, and 76 are responsible for the more intense fatty, cardboard-like and ink-like phenolic odor in SL and AL compared to VL (figure 1-3).

TABLE I
Identified odorous substances and their flavor-dilution-factors of sole leather (VL), automotive leather (AL) and shoe upper leather (SL).

No.	Compound[a]	Flavor quality[b]	BL	AL	VL
2	Methyl propane acid ethyl ester	fruity	4	1	< 1
4	2-methyl butyric acid ethyl ester	fruity	4	8	4
5	3-methyl butyric acid ethyl ester	fruity	1	4	2
6	hexane	grassy, green	32	32	64
8	(Z)-3-hexenale	grassy, green	< 1	32	< 1
9	heptanale	soapy	< 1	4	2
11	(Z)-4-heptenale	fishy, oily	4	32	64
12	octanale	citric-like, green	32	32	128
13	1-octen-3-on	fungoid	4	4	32
14	dimethyltrisulfid	cabbage-like	< 1	2	4
15	(Z)-1.5-octadien-3-one	geranium-like	< 1	4	< 1
16	nonanale	citric-like	16	8	32
17	3-isopropyl-2-methoxypyrazine	earthy, pea-like	< 1	8	< 1
18	(Z)-4-nonenale	fatty	128	16	128
20	acetic acid	vinegar-like	4	16	2
21	(Z)-2-nonenale	fatty, green, cardboard-like	256	256	256
22	3-isobutyl-2-methoxypyrazine	capsicum-like	256	16	< 1
23	(E)-2-nonenale	fatty, green, cardboard-like	1024	256	256
25	(E,Z)-2,6-nonadienale	like cucumber	256	256	64
26	(Z)-2-decenale	fatty	1	< 1	64
27	unknown	fatty	1	8	4
28	butyric acid	sweaty	64	16	8
29	(E,Z)-2.4-nonadienale	fatty, green	4	8	128
30	2-hydroxybenzaldehyde	band-aid	32	32	1
31	2-/3-methyl butyric acid	sweaty	< 1	8	16
32	unknown	fatty	< 1	<1	16

Table I continues on following page.

Table I continued.

33	(E,E)-2.4-nonadienale	fatty, green	1	32	64
35	valeric acid	sweaty, fruity	8	2	2
36	(E,Z)-2.4-decadienale	fatty, deep-fried	8	< 1	32
37	2,4,6-trichloranisole	moldy, musty	2	16	8
38	(E,E)-2.4-decadienale	fatty, deep-fried	4	< 1	64
40	hexanoic acid	sweaty	< 1	4	1
41	2-methoxyphenol	smoky, sweetish	1,024	64	64
42	(E,E,Z)-2.4.6-nonatrienale	black tea	32	128	64
44	γ-octalacton	coconut, musty	4	32	32
45	Benzothiazole	rubber-like, coal	8	16	8
46	5-methyl-2-methoxyphenol	smoky, clove	1,024	< 1	< 1
50	(E)-4.5-epoxy-(E)-2-decenale	metallic	4	128	256
51	Phenol	ink, phenolic	32	< 1	< 1
52	γ-nonalacton	coconut	4,096	128	512
53	4-ethyl-2-methoxyphenol	smoked	256	< 1	< 1
54	4-hydroxy-2.5-dimethyl-3(2H)furanon	caramel-like	32	< 1	< 1
58	4-methylphenol	fecal, phenolic, horse stable	128	64	32
59	unknown	spicy	< 1	4	< 1
60	unknown	fishy, like sea	64	16	< 1
61	unknown	leather-like	< 1	< 1	< 1
62	4-allyl-2-methoxyphenol	clove	4,096	64	8
63	4-ethylphenol	phenolic	16	1	2
65	unknown	ink-like, medical	< 1	512	256
66	δ-decalacton	peach, coconut	32	8	< 1
67	3-hydroxy-4.5-dimethyl-2(5H)furanone	lovage, spicy	512	64	64
68	unknown	citric-like, coconut	8	32	< 1
69	2.4.6-tribromanisol	moldy, musty	16	128	16
70	2.6-dimethoxyphenol	smoky, sweet, clove	128	2	< 1
71	unknown	musty	2	4	< 1
72	unknown	musty	16	< 1	< 1

Table I continues on following page.

Table I continued.

73	2-(methylthio-)benzothiazol	medical, rubber-like	8	< 1	< 1
76	4-chloro-3-methylphenol	ink, phenolic	< 1	1,024	256
77	phenyl acetic acid	beeswax, honey	1,024	16	16
78	vanillin	vanilla, sweet	4,096	64	256
79	2-phenylphenol	sweetish, plastics	< 1	2	< 1

[a]The compounds were identified through comparison of the linear retention indices at the capillary columns DB-FFAP and DB-5, of the odor qualities as well as the mass spectrums (MS-EI) with the properties of the reference compounds — unless otherwise stated. [b]Odor quality of the compound which was detected during smelling. [c]RI: linear retention index of the compound at the capillary columns DB-FFAP and DB-5. [d]Aroma dilution (FD) factor, determined through aroma extraction-dilution analysis; odorous substances with an FD factor ≥ 4 in at least one sample are listed. [e]The obtained mass spectrum was too weak for a clear identification. For this reason the structure of the compound was clarified on the basis of the remaining identification criteria (see footnote a).

TABLE II
Concentrations (in µg/kg) of odorous substances in sole leather (VL), automotive leather (AL) and shoe upper leather (SL).

No.[a]	Compound	BL [b]	AL [b]	SL [b]
6	hexane	96.5	1,750	2,670
11	(Z)-4-heptenale	< 2,4	14.4	9.7
12	octanale	96.4	169	285
13	1-octen-3-on	< 0.2	3.6	5.6
16	nonanale	127	399	732
20	acetic acid	74,200	67,400	34,700
23	(E)-2-nonenale	199	489	172
25	(E,Z)-2.6-nonadienale	40.2	174	20.4
28	butyric acid	3,480	< 1,370	624
30	2-hydroxybenzaldehyde	280	27.4	15.9
31	2-/3-methyl butyric acid	< 154	< 151	< 157
33	(E,E)-2.4-nonadienale	17.7	196	95.5
35	valeric acid	1,280	387	173
38	(E,E)-2.4-decadienale	34.5	298	164
40	hexanoic acid	3,300	5,660	1,670

Table II continues on following page.

Table II continued.

41	2-methoxyphenol	140	1.3	9.6
44	γ-octalacton	34.6	184	72.1
45	benzothiazole	69.4	190	472
46	5-methyl-2-methoxyphenol	24.3	< 2.1	< 2.1
50	(E)-4.5-epoxy-(E)-2-decenale	< 1.4	5.6	16.5
51	phenol	40,500	838	1,860
53	4-ethyl-2-methoxyphenol	468	< 2.3	< 3.4
58	4-methylphenol	119	21.6	25.4
62	4-allyl-2-methoxyphenol	137	209	100
70	2.6-dimethoxyphenol	402	112	19.9
73	2-(methylthio-)benzothiazole	< 0.64	20.5	13.0
76	4-chloro-3-methylphenol	15.5	299,000	14,000
78	vanillin	590	87.2	158
79	2-phenylphenol	26.5	132,000	4,810
52	γ-nonalacton	154	307	116
54	4-hydroxy-2.5-dimethyl-3(2H)furanon	41.9	< 16.6	< 16.6
67	3-hydroxy-4.5-dimethyl-2(5H)furanon	4.7	1.9	1.2

[a]Numeration refers to table 3. [b]the values stated are the arithmetic average from a minimum of three single calculations, the relative standard deviation was < 10%.

TABLE III
Odor thresholds and aroma values of key odorous substances in sole leather (VL), automotive leather (AL) and shoe upper leather (SL).

No.[a]	Compound	GS[b]	BL[c]	AL[c]	SL[c]
6	hexane	5.9	16	297	452
11	(Z)-4-heptenale	0.43	< 1	33	23
12	octanale	8.4	11	20	34
13	1-octen-3-on	0.18	< 1.2	20	31
16	nonanale	51	2.5	7.8	14

Table III continues on following page.

Table III continued.

23	(E)-2-nonenale	1.2	166	408	143
25	(E,Z)-2.6-nonadienale	1.2	34	145	17
30	2-hydroxybenzaldehyde	34	8.2	< 1	< 1
33	(E,E)-2.4-nonadienale	6.6	2.7	30	14
37	2.4.6-trichloranisol	0.050	< 29	< 29	< 29
38	(E,E)-2.4-decadienale	4.1	8.4	73	40
41	2-methoxyphenol	6.3	22	< 1	1.5
44	γ-octalacton	31	1.1	5.9	2.3
45	Benzothiazole	53	1.3	3.6	8.9
46	5-methyl-2-methoxy-phenol	4.7	5.2	< 1	< 1
50	(E)-4.5-epoxy-(E)-2-decenale	16	< 1	< 1	1.0
51	phenol	5,700	7.1	< 1	< 1
52	γ-nonalacton	13	12	24	8.9
53	4-ethyl-2-methoxyphenol	23	20	< 1	< 1
54	4-hydroxy-2.5-dimethyl-3(2H)furanon	95	< 1	< 1	< 1
58	4-methylphenol	13	8.7	1.7	2.0
62	4-allyl-2-methoxyphenol	370	< 1	< 1	< 1
67	3-hydroxy-4.5-dimethyl-2(5H)furanon	18	< 1	< 1	< 1
69	2.4.6-tribromanisol	0.20	< 7	< 7	< 7
70	2.6-dimethoxyphenol	1,200	< 1	< 1	< 1
73	2-(methylthio-) benzothiazol	350	< 1	< 1	< 1
76	4-chloro-3-methylphenol	1,300	< 1	230	11
78	vanillin	150	3.9	< 1	1.1
79	2-phenylphenol	18,000	< 1	7.3	< 1

[a]Numeration see table 1. [b]GS: orthonasal odor threshold in gelatin. [c]The aroma value is calculated as quotient of the concentration of a compound and the orthonasal odor threshold in gelatin (Rothe and Thomas, 1963).

Simulation of the Leather Odors

The aroma profile detected was validated by simulation of the leather odors and the comparison with the odor of the original leather.

For this purpose the leather odorous substances were solved in a matrix in the determined concentration ratios. An oil-in-water emulsion (5% fat) proved to be suitable for this purpose. The odorous substances were added to these emulsions and

TABLE IV
Similarity assessment of the odor profile of leathers and their odor simulations.

Leather	Similarity ranking[a]
sole leather	1.8
automotive leather	2.1
shoe upper leather	2.2

[a]The similarity of the leather samples and the odor simulations were assessed on a scale from 0 (no similarity), 1 (slight similarity), 2 (clear similarity) to 3 (identical).

after shaking underwent an aroma profile analysis. Table 4 shows the similarity ranking of the leather odors of AL, VL and SL with the corresponding odor simulations. The odor profiles proofed to be nearly identical. Thus, the correctness of the experimental approach was proven. The corresponding leather odor could be reflected by the leather odor substances determined.

Influence of Production Processes on the Leather Odor
The importance of production processes for the leather odor was examined on the example of a chrome-tanned leather. The pelt was tanned with chrome and preserved under defined conditions and afterwards retanned and fatted. Samples of the Wet Blue (WB), the retanned Wet Blue (RT) and the fatted leather (FL) were removed after the individual process steps and examined for odorous substances the same way as the leather samples. It was found that the WB differed more from the RT and the FL with regard to the odor than the RT from the FL.

Table 5 shows the concentrations, the odor thresholds and the aroma values of the odor-relevant substances after the individual technological steps have been performed. Due to re-tanning the concentrations of odorous substances are partly influenced considerably. Thus, very significant differences in the total odor of Wet Blue and re-tanned Wet Blue are caused. In particular, this applies for 4-chloro-3-methylphenol, which lost in odorous activity through leaching during re-tanning. Fatting of the leathers does also result in changes in the odorous substances contents which however were not that sensory relevant in these samples.

Examination of the Influence of Leather Additives on Leather Odorous Substances
These examinations were to distinguish whether the sources of the odorous substances are already available in the additives or they are formed from odorless preliminary stages. For this purpose the concentrations of selected odorous substances in the re-tanning agents Basyntan SL, Basyntan SW, Relugan RV, Tamol M, Tamol Na and Tara, and in the fat liquors Lipoderm liquor A1 and Lipoderm LA were quantified using the stable isotope dilution analysis.

Only small quantities of odorous substances were found in the six re-tanning agents (exceptions: octanale and vanillin). It can be concluded from the results that the most important leather odorous substances such as hexane, 1-octen-3-on, (E,Z)-2.6-nonadienal, (E,E)-2.4-nonadienal and p-anisaldehyde are not contained in the re-tanning agents, but are formed from odorless preliminary odorous substance stages during re-tanning.

However, large quantities of the odorous substances hexane, octanale, g-octalactone and g-nonalactone (1,090 to 61,700 μg/kg) were determined in the two fat liquors. Thus, fat liquors contribute to the leather odor also directly. However, due to the oxidative reduction of fats there is always the possibility of forming odorous substances from odorless preliminary stages.

Development of Emission-Analytical Rapid Methods for Assessing the Leather Odor
Knowing the key odorous substances and the aromas' composition it was tried to specifically detect these substances using emission-analytical methods. The emitted odorous substances were quantified via calibration, in order to compare the relative contributions with those of the aroma analysis.

The following sampling methods were applied:

- Direct Thermal Desorption
- Static Headspace
- External adding to Tenax® with subsequent thermal desorption

External adding with subsequent thermal desorption proved to be the most suitable method. Extractions were performed at 50°C and 100°C. When applying the other methods sections of the substance spectrum were suppressed and the maximum substance quantity of the substances transferrable to the GC was limited, so that substances with very low concentration and low odor thresholds were not gathered.

Figures 4 and 5 illustrate this with the chromatograms after parallel detection at the ODP and mass spectrometer.

The quantity of the substances thus transferrable to the column is very high which results in overlapping in the chromatogram. Otherwise, not all odor-relevant substances are detected in the chromatogram. A number of these substances are below the so-called "Ölberg", which is characteristic for an emission spectrum of leather. Therefore a useful evaluation was possible

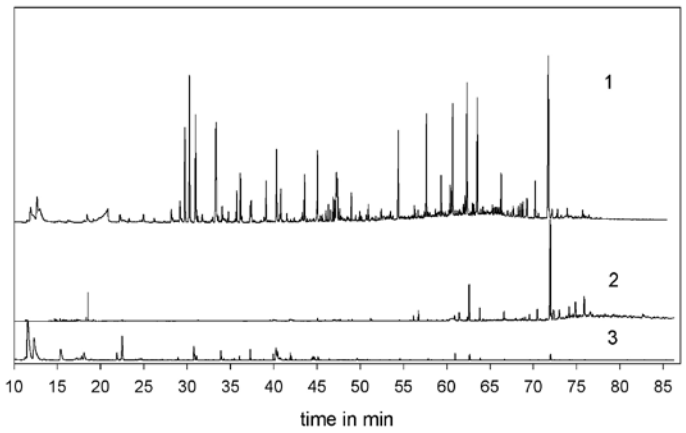

Figure 4. Chromatograms based on different extraction methods (detector: mass spectrometer)
1: External adding to Tenax®+ thermal desorption (3g, 50°C, 3h)
2: Thermal desorption (0.05g, 20°C, 0.5h)
3: Headspace (3g, 120°C, 5h)

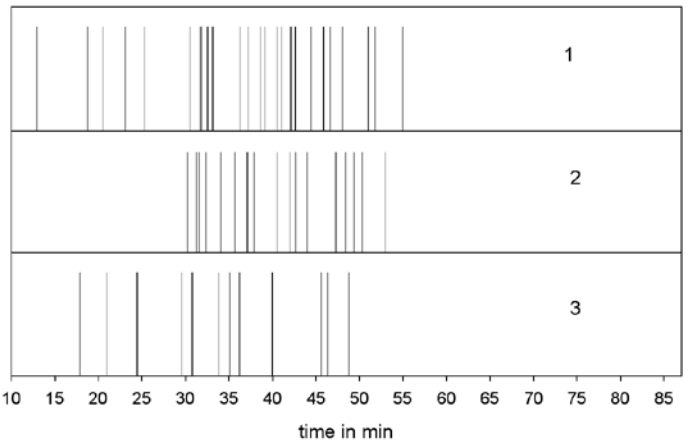

Figure 5. Chromatograms of the odor occurrences based on different extraction methods (detector: Olfactometric Detection Port).
1 External adding to Tenax® + thermal desorption (3g, 50°C, 3h)
2: Thermal desorption (0.05g, 20°C, 0.5h)
3: Headspace (3g, 120°C, 5h)

in SI-mode (single ion) only. The quantitative evaluation was performed after calibration using the key odorous substances with aroma values showing a respective contribution to the odor.

Figure 6 shows the comparison between the aroma values, the substance concentrations in leather and the concentrations of emission measurements determined using the example of automotive leather.

At an extraction temperature of 100°C all odor-relevant substances could be detected via emission, however the intensity ratios of the substances determined by means of emission-analysis do not reflect the ratio of the aroma values. The concentration ratios of the substances in leather are reflected a bit better, however they do not correspond to the emission values.

This is partly due to the fact that the emitted quantity of a substance depends on its volatility, concentration in leather and interactions within the matrix. In addition, the aroma value includes the odor threshold, so that the actual contribution of a substance to the odor cannot be reflected by quantification of the emitted quantity of the substance only.

This demonstrated the limits of the emission-analytical methods for the characterization of complex odors, which could have similar qualitative composition and differ only by a varying quantitative composition.

Discussion and Conclusions

By combination of sensory and analytical methods the odor-relevant compounds of different leather types could be determined for the first time. These odorous leather substances were clearly identified and quantified. The respective leather odors could be successfully simulated.

Different leather types have different odors. Varied characteristic odorous substances cause these very significant sensory differences. Unsaturated aldehydes and phenolic compounds were detected to be the source of aroma defining the vegetable-tanned sole leather. In automotive and shoe upper leather, preservative agents as well as saturated and unsaturated aldehydes were found to be aroma defining…? That is why different leather odors are generated by different odorous substances as well as by the different compositions of the same odorous substances.

The following substance groups are involved in forming the leather odor:

- Aldehydes and lactones fat liquors and their degradation products
- Phenolic compounds from vegetable tanning and re-tanning agents
- Halogenated phenols, 2-phenylphenol and benzothiazole originate from preservative agents and their reaction products

Upon close examination of the production process, it showed that re-tanning essentially determines the defining odor of the leather product. In particular, this is caused by the considerable reduction in odor-defining preservative substances which presumably due to simple leaching out of the leather during re-tanning. In contrast, the concentrations and thus the importance of unsaturated aldehydes in the odor of the re-tanned leather increased. Reason for this can only be the

TABLE V.
Concentrations, odor thresholds and aroma values in Wet Blue (WB), re-tanned Wet Blue (RT) and fatted leather (FL).

No.[a]	Compound	Concentration[b] (µg/kg) in			GS[c]	Aroma value[d] in		
		Wet Blue	RT	FL		Wet Blue	RT	FL
6	hexane	49.6	176	349	5.9	8.4	30	59
12	octanale	38.6	73.4	111	8.4	4.6	8.7	13
13	1-octen-3-on	< 0.2	4.1	5.7	0.18	< 1.2	23	32
23	(E)-2-nonenale	12.5	55.3	142	1.2	10	46	118
25	(E,Z)-2.6-nonadienale	< 1.7	19.6	13.0	1.2	< 1.4	16	11
33	(E,E)-2.4-nonadienale	1.8	24.4	67.0	6.6	< 1	3.7	10
41	2-methoxyphenol	2.2	4.6	5.7	6.3	< 1	< 1	< 1
58	4-methylphenol	74.2	69.4	85.0	13	5.7	5.3	6.5
76	4-chloro-3-methylphenol	1,520,000	294,000	637,000	1,300	1,170	227	490
78	vanillin	18.8	260	469	150	< 1	1.7	3.1
79	2-phenylphenol	630,000	151,000	377,000	18,000	35	8.4	21
88	p-anisaldehyde	< 15	212	184	120	< 1	1.8	1.5
44	γ-octalacton	17.3	43.4	157	31	< 1	1.8	6.5
52	γ-nonalacton	35.9	69.4	559	13	2.8	5.1	43
45	benzothiazol	302	411	445	53	5.7	7.7	8.4
69	2.4.6-tribromanisol	2.2	1.8	5.1	0.20	11	9.0	26

[a]Numeration refers to table 9. [b]The values stated are the arithmetic average from a minimum of three single calculations, the relative standard deviation was < 10%. [c]GS: orthonasal odor threshold in gelatin. [d]The aroma value is calculated as the quotient of the concentration of a compound (tab. 11) and their orthonasal odor threshold in gelatin (Rothe and Thomas, 1963).

formation of odorous substances from odorless preliminary stages (e.g. unsaturated fat acids). The additives contain only small quantities of odorous leather substances, so that they are not primarily odor defining. However, it could be shown that some odorous substances pass from the fat liquors to the leather.

For a specific influence on the leather odor during the leather production, there is no formula concerning the use of defined leather additives for defined odors due to the complexity of the leather odor and the universality of important odorous components. Though a clear influence of the quantity of preservative agents used is proven.

Due to the complexity of the leather odor, the composition of the same cannot be reflected by using emission-analytical methods in a satisfactory way.

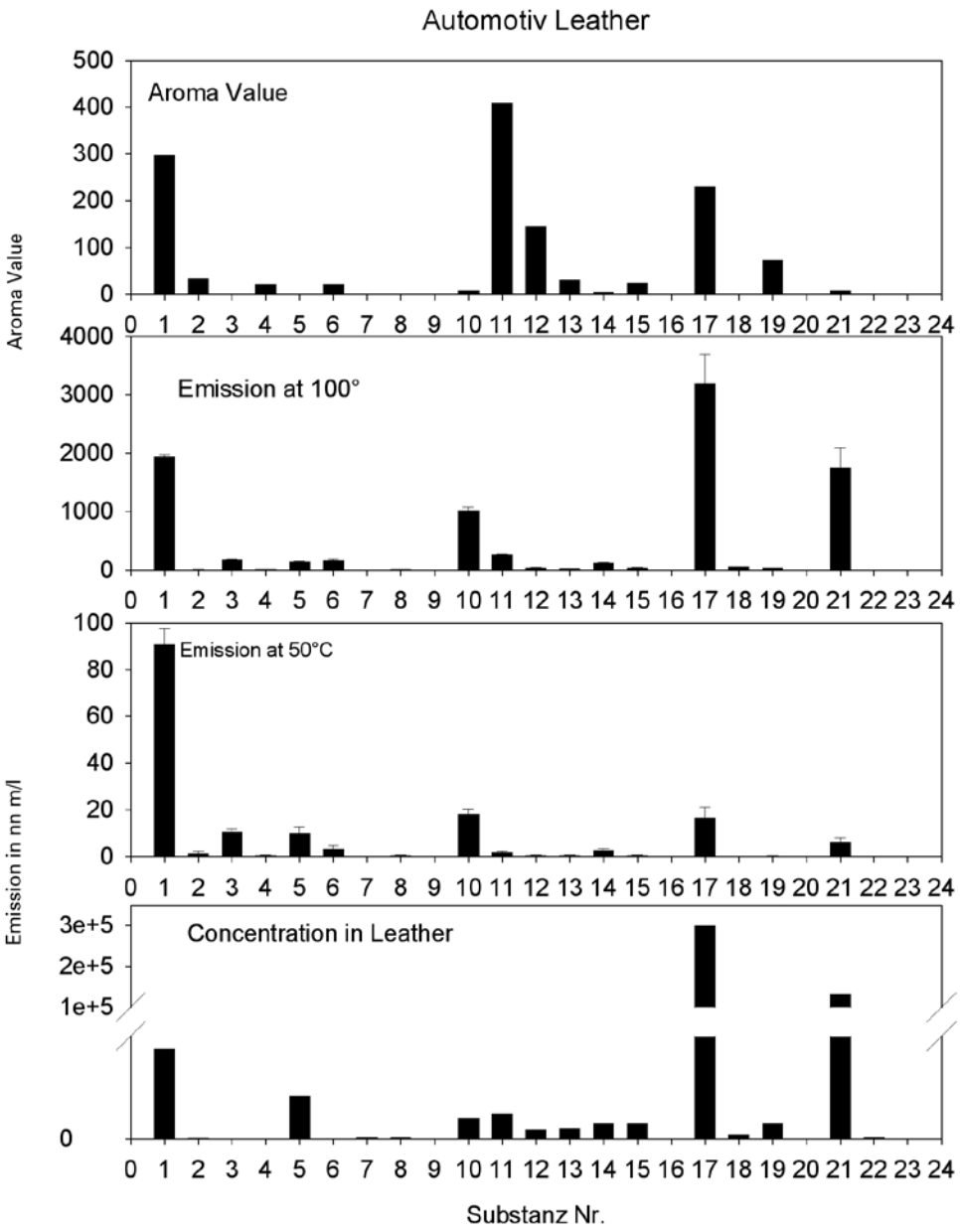

Figure 6. Comparison of the concentrations, aroma values of intense odorous substances with the emission values at 50°C and 100°C (external adding) of automotive leather.

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