

Identification of volatile compounds the vegetable tanned leather

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SUMMARY

The vegetable tanned leather is very famous for the its wonderful and unmistakable odour. In general terms the odour can be defined as any emanation perceived by sense of smell; practically the odorous substances have to be sufficiently volatile for being inhaled and for coming to be counted with the receptors of the nasal mucosa. In other words, the odour is connected to the emanation of volatile substances, therefore the knowledge of such substances can contribute to define the responsible components of the perceived odour.

In a previous research, it has been demonstrated that the gas-chromatography with a mass spectrometer detector (GC/MS), coupled to the Purge & Trap technique, is a valid analytical approach for the identification of volatile compounds in the leather.

Therefore in this study, such technique has been employed for the study of the volatile substances rising from vegetable tanned leathers. The investigations have been turned to leather goods, classified according to type of article (leather sole, fattened vachette, etc.).

INTRODUCTION

The aim of this work is to characterise the volatile substances present in vegetable tanned leathers, in order to identify the substances responsible of their typical odour.

The volatile substances are responsible for important organoleptic properties of the leather product such as the smell, characterising not just the quality of the article, intentional and pleasant smells, but in some cases imperfections connected with bad smells. In short, for leather material the ideal is to have a perceptible but not strong smell so as not to be overly disturbing.

But what is smell? A smell may be defined as any emanation perceived through the sense of smell.

An essential condition therefore for a smell to be perceived is that it can be “smelt”; in practice this means that the odorous substances must be in an aeriform state so as to be inhaled and come into contact with the olfactory receptors of the nasal mucous membrane.

For the assessment and determination of the intensity of a smell, for quality control or olfactory disturbance, the olfactometer is generally used. This consists of the sensorial analysis of an

osmogen “panel test” mixture, which is presented to a jury of selected persons (panel), and the processing of the results obtained. This olfactory panel test is today regulated by a European technical regulation, the EN 13725 for the standardisation of olfactometric analysis.

Unlike chemical analysis, olfactometric analysis does not provide the identification of a substance or group of substances, but the units of odour of the gaseous mixture: this way the olfactory impact can be calculated, although remaining a subjective sensation. By knowing the number of dilutions required for the smell to be perceived by the panel, the number of units of odour per cubic metre of the examined sample is calculated. This measurement technique permits an evaluation of the possible synergic and masking effects too so that the concentration of smell (OU/mc) of a mixture of compounds is not the algebraical sum of the single substances but the result of more complex phenomena and relations. The instrument which makes it possible to carry out the right dilutions is the olfactometer, by means of which the group of panellists judges the perceptibility of the sample. This investigation method, while useful for the purposes of assessing the olfactory-disturbance impact of a gaseous mixture and for commercial purposes given that it provides hedonistic information about a product, does not however permit the identification of the various compounds causing the smell within the gaseous mixture constituting the smell, nor their quantitative evaluation.

This study conducts a broad investigation for the qualitative-quantitative definition of the odour of leather or of other “tannery” smells using analytic-instrumental methods so as to define the characteristics in an objective manner but also to identify the possible causes of olfactory disturbance in some vegetable tanned leather articles. Against such advantages however it is presumable that these methods will have the disadvantage of a reduced sensitivity compared to the human “instrument” in detecting some compounds to which the sense of smell is particularly sensitive (very low threshold for the perception of the smell), especially in the case of mixtures of substances which together produce smells that are particularly difficult to reproduce in the laboratory or to associate with one or a group of chemical substances.

The technical scientific approach was that of extracting the volatile substances from the leather using the “purge and trap” technique which consists of stripping the substances from the sample at a controlled temperature using a flow of inert gas (helium) which strips off and transports the volatile substances to an absorbent trap where they are concentrated to then be thermally desorbed and channelled to a gas-chromatography system connected to a mass detector for the resolution of the volatile mixture and the identification of each single volatile component.

This technique enhances the result of the analysis of the volatile substances present in traces unlike another commonly used sampling technique, the “static head space”, which only enables the

detection of the most plentiful substances and present in a concentration determined by the equilibrium with the sample and the environment with which it is in contact.

The work, moreover, permitted the creation of a sort of identificatory “spectrum” of the skins represented by the gas-chromatogram showing the volatile substances eluted, a sort of leather identity card, depending on the article (e.g. upper, clothing, furnishings) and in perspective, before a long series of characterisations, on the tannery district of provenance.

EXPERIMENTAL

The analyses have been carried out on full vegetable tanned leather, intended for use as sole, upper and leatherwear. In the following list

Tannery	Code	Description
A	A1	Natural sole leather
	A2	Standard finished sole leather
B	B1	Nubuk butt sole
	B2	Full grain butt sole, with superficial application of wax
C	C1	Fattened vachette
D	D1	Finished upper leather fattened by tallow
E	E1	Natural like leather for uppers, leatherwear and belts production
	E2	Pigmented like leather for uppers, leatherwear and belts production
	E3	Fattened vachette like leather for uppers, leatherwear and belts production
	E4	Grinded and pigmented leather for leatherwear

A sample, of each type of skin mentioned above, with dimensions equal to $3 \times 3 \text{ cm}^2$ was cut into pieces of approximately $0.3 \div 0.4 \text{ cm}^2$ and put into a glass container (vassel) closed hermetically inside the “purge and trap” system.

The sample was then heated with an infrared lamp to a temperature of 50°C , so as to speed up the removal of the volatile substances (kinetic effect). In the “purge and trap” phase the substances are stripped using a flow of helium at approximately 40 ml/min for a period of 20 minutes and then forwarded to the absorbent trap type T10 (TENAX / Silica gel / carbon molecular sieve) kept at room temperature.

The system then automatically activates the thermal desorption phase of the substances in the trap at a temperature of 190°C , to then direct them to the gas-chromatograph, fitted with a column input

system, the high temperature split/splitless, by means of a heated transfer line, thus avoiding the condensation of some less volatile component. At the exit of the gas-chromatograph the eluted components are directed to a quadruple type mass detector which, by the use of a dedicated software and a sufficient library of mass spectrums of chemical substances, enables their identification and consequently the characterisation of the mixture of volatile substances emitted by the leather. Below are the sampling and analysis conditions adopted:

Purge and trap system Analytical mod. ECLIPSE 4 F3390 :

Purge: transport gas = helium flow = 40 ml/min
temperature = 50 °C;
time = 20 min;
trap temperature = 20 °C;
Desorb: temperature = 190 °C;
time = 2 min;

Gas-Chromatographic System	GC/MS HP mod. 6890 Series and 5973 Mass Selective detector
Injector	Split/splitless
Transport Gas	Helium
Flow	1 ml/min
Injector Temperature	280 °c;
Split Ratio	10/1
Temperature Programme:	40 °C for 5 min. Then Ramp at 5 °C/min. Until 200 °C Ramp at 10 °C/min. Until 250 °C hold for 5 min.
Column	Superchrom DB1 L=60m; ID=0,25mm; F=1mm
Detector	Quadrupole MS detector type HP mod.

An example of the chromatograms obtained with this operative conditions, is reported in Figure 1. It is relative to the analysis of the samples C1 and shows the identifications made by the mass detector of the volatile substances, where the number, reported in brackets alongside the name, gives the percentage of recognition.

RESULTS AND DISCUSSIONS

From the analysis of the gas-chromatography results, specific families of volatile organic compounds can be identified and they or the single compounds can be associated with the leather article produced, the animal origin of the leather and lastly the state of the leather (pickled, wetblue, crust, finished).

The compounds identified were then grouped into the following families:

- Aldehydes

- Alcohols
- Ketones
- Esters
- Etero compounds
- Furanes
- Paraffinic and olefinic hydrocarbons
- Aromatic hydrocarbons
- Polycyclic aromatic hydrocarbons

In table 1, the results of analyses of the volatile emission of sole leathers are reported.

Table 1. Volatile emission of investigated sole leathers

Compound family	Code			
	A1	A2	B1	B2
Aldhehydes	0,2%	0,0%	1,0%	1,0%
Alcohols	17,4%	19,6%	1,0%	19,5%
Ketones	14,1%	15,6%	2,2%	5,0%
Esters	21,0%	5,2%	51,9%	56,9%
Etero compounds	39,4%	48,4%	0,5%	1,1%
Paraffinic and olefinic hydrocarbons	0,9%	3,5%	3,6%	8,6%
Aromatic hydrocarbons	6,5%	7,5%	39,7%	7,3%
Polycyclic aromatic hydrocarbons	0,6%	0,2%	0,0%	0,5%

We can point out that the volatile emission of leathers deriving from tannery A exhibits an high content of etero-compounds, due, in both cases, mainly to the presence of sulphur dioxide. This evidence can be explained with the wide use of sulphite or bisulphite salts of vegetable extracts in tanning.

For the leathers of tannery B, the VOCs are mainly constituted by esters, that represent over 50% of total volatile fraction, in terms of percent area. Butyl acetate, with its peculiar pear odour, is the main component of esters, and its use is due to the considerable solvent effect on resins.

In table 2 the results of analyses, carried out on the vegetable tanned leathers intended for uppers and leatherwear productions, are listed:

Table 2. Volatile emission of investigated vegetable tanned leathers intended for uppers and leatherwear productions

Compound family	Code					
	C1	D1	E1	E2	E3	E4
Aldhehydes	12,4%	3,2%	8,3%	2,1%	2,9%	5,8%
Alcohols	7,0%	11,0%	30,9%	26,3%	20,2%	24,2%
Ketones	25,9%	2,5%	7,8%	5,7%	26,0%	5,2%
Esters	27,3%	0,9%	23,7%	26,3%	12,1%	23,9%
Etero compounds	3,7%	1,6%	2,0%	9,2%	9,3%	11,7%
Furanes	0,2%	0,0%	0,6%	0,5%	1,6%	0,0%
Paraffinic and oleofin hydrocarbons	12,7%	77,9%	11,2%	13,7%	11,5%	14,2%
Aromatic hydrocarbons	8,8%	1,0%	14,7%	14,7%	13,4%	13,6%
Polycyclic aromatic hydrocarbons	2,0%	1,7%	0,9%	1,4%	3,0%	1,4%

The volatile emission of fattened vachette (sample C1) is characterized by VOCs of esters and ketones families, than represents over the 50% of volatile emission. A contribution to the typical odour of such type of article is surely supplied from volatile compounds of aldehydic nature (12,4%), whose main member is the hexanal which has a characteristic odour of fat, in particular of tallow. The presence of aldehydes is due to the use of essential oils in the fatliquoring stage, but probably also to the retanning products, as residues of synthesis (untransformed reagents). This consideration has been supported, in a previous work on chrome tanned leathers, by the fact that the relative integration areas of the peaks corresponding to the aldehydes decreases in percentage terms if we analyze leathers from the crust to the finished state, deriving from the same process. The sample D1, reported as finished upper leather fattened by tallow, shows an high fraction of aliphatic hydrocarbons (77,9%). Also compounds of alcohol class, mainly ethanol and butylglycol, are present in not negligible amount (11%).

As to the other investigated samples, all produced by tannery E, the main constituents of volatile emissions are the alcohols, aldehydes and aliphatic and aromatics hydrocarbons. The methoxypropanol, with slight ethereal odour, is the main component of the volatile emission of all the leathers deriving from tannery E, while, also in these cases, the butyl acetate results to be the most important component of esters.

CONCLUSIONS

In this study it has been seen how the Purge and Trap investigation technique used with gas chromatography and the mass detector is useful in identifying the volatile organic substances emitted by vegetable tanned leathers.

The cognitive surveying on the volatile matter has substantially evidenced that:

- the sulphur dioxide, probably deriving from sulphitation of vegetable extracts, is the main component in some sole leathers, and therefore it can have an influence on their characteristic odour:
- the typical odour of fattened vachette could be due to volatile compounds of aldehydic nature, and in particular to the hexanal, reported to have a characteristic odour of tallow in literature;
- the volatile emission of the other leathers, intended for uppers and leatherwear productions, presents many classes of compounds, such as alcohols, esters and hydrocarbons, supposedly deriving from retanning or finishing steps of production.

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Sample C1 FATTENED VACHETTE

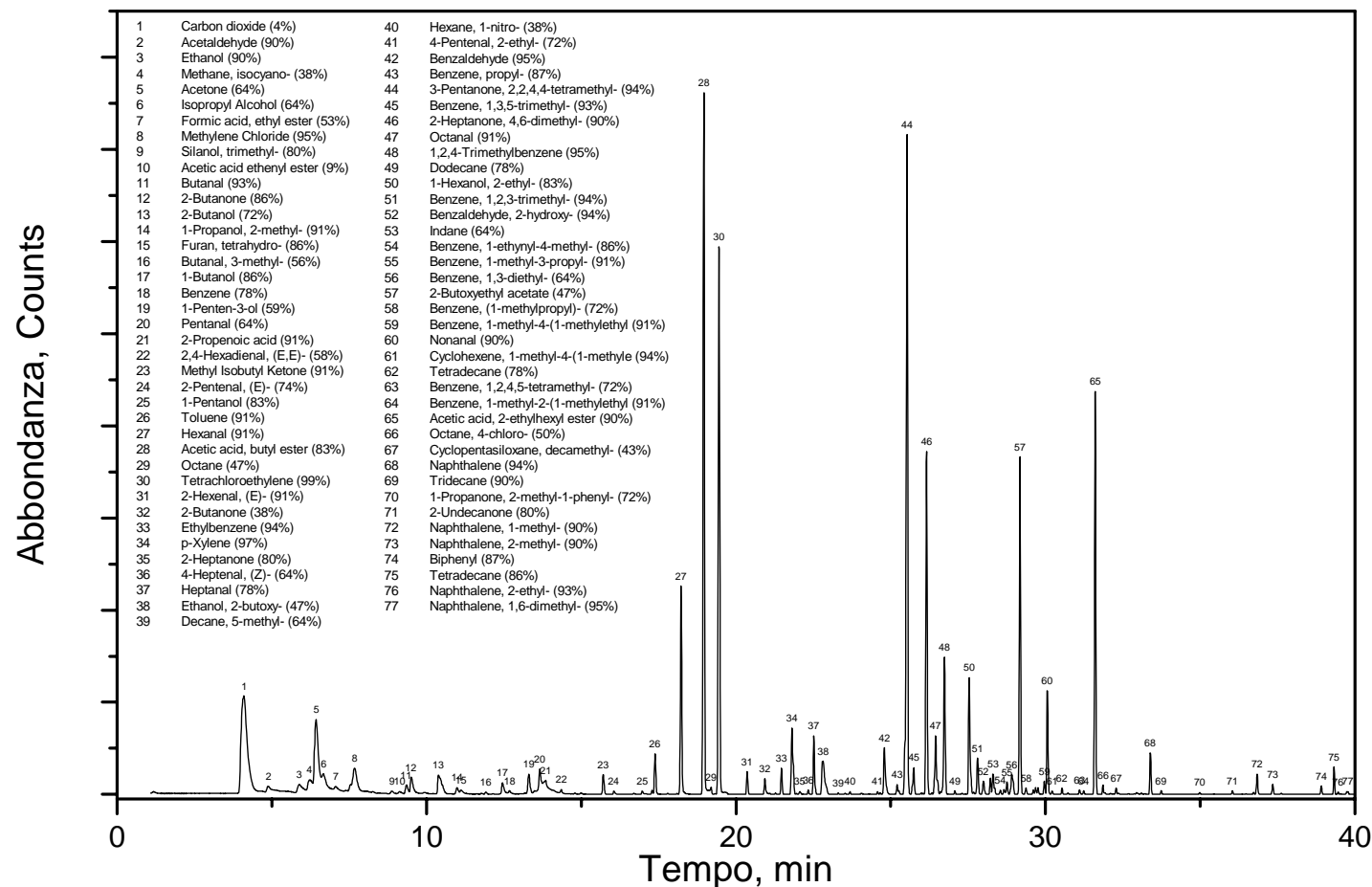


Figure 1. GC-MS chromatogram of volatile emission of sample C1