THE CHARACTERIZATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN WET-WHITE AND METAL FREE LEATHER

Naviglio B[1]., Florio C.[1], Caracciolo D.[1], Gambicorti T.[1], Aveta R.[1], Girardi V., Scotti M.[1]

1 Stazione Sperimentale Industria Pelli e Materie Concianti, Via Campi Flegrei, 34, 80078 - Pozzuoli - NA

Phone: 39-081-5979100, Fax: 39-081-265574

Corresponding author: c.florio@ssip.it; t.gambicorti@ssip.it

Abstract. In recent years, among the tanning sector, the so-called wet-white and/or metal-free concepts have had a certain increase. For example, in the automotive sector the wet-white tanning system, carried out with glutaraldehyde and tannins, has had widespread use. Automotive manufacturers, indeed, offer leather for interior furnishings not only for luxury cars but also in lower market segments. The components on which the leather upholstery is applied are mainly steering wheel, seats, dashboard and panels. Therefore, the use of leather also in this context must be able to meet both the aesthetic/performance criteria and the environmental ones; environmental criteria should also consider the air quality of the interior of a motor vehicle. In practice, the interior furniture consisting of finished leather should have to be able to release a few volatile substances and, at the same time, provide a typical smell of leather. Considering, therefore, the diffusion of alternative chrome tanning systems for the different uses, in this work, wet-white (glutaraldehyde and tannins) will be investigated, both from the point of view of the performance characteristics and from the ecotoxicological ones. Furthermore, leathers deriving from the latest generation of metal-free tanning, will be analysed. For the characterization of Volatile Organic Compounds (VOC) the GC-MS will be used coupled with the "Purge and Trap" technique with the aim of obtaining information on the new substances used in the wet-white / metal free production process and then avoiding undesired effects during use (eg bad smell, SVHC substances, etc.)

1 Introduction

Recently, an increase in the spread of leather tanned with alternative chrome systems and marketed under different names such as "wet-white", "chrome-free", "metal-free", etc. has been observed on the market; for example in the automotive sector the wet-white tanning system, carried out with glutaraldehyde and tannins, has had a widespread use.

In order to characterize these types of leathers (wet-white and latest generation tanning), various analytical investigations have been carried out to evaluate the presence of tanning metals and Volatile Organic Compounds (VOCs).

The evaluation of the tanning metals allowed to better define the type of tanning according to the current European Standard (EN 15987:2015) while the VOCs allowed to obtain information about any undesired effects concerning the bad smell and the possible presence of SVHC substances.

2 Materials and methods

The following leather samples have been analysed:

1. Bovine crust chrome tanned leather for automotive use
2. Bovine wet-white tanned crust leather for automotive
3. Bovine dyed crust leather tanned with latest generation of organic tanning for automotive
4. Sheep not dyed crust leather tanned with latest generation of organic tanning for leather goods

The bovine leathers were supplied by an Italian tannery of the Veneto district while the ovine one comes from the Solofra district. The samples were analyzed with the following instruments:

- *HP GC System/6890 - HP/5973 Mass Selective* Chromatograph equipped with a Purge & Trap *O.I.Analytical 4660* Sampler.
- *Thermo Fisher - ICAP RQ* -Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

3 Results and discussion

3.1 Tanning metals

Table 1 shows the analytical results relating to the tests carried out to evaluate the chemical characteristics of the samples, in order also to define the type of tanning in accordance with the standardize terminology of leather (EN 15987 European Standard).

Tab. 1. Chemical characteristics of the examined leathers

Parameter	Method	Sample 1 *Bovine crust chrome tanned leather for automotive*	Sample 2 *Bovine wet-white tanned crust leather for automotive*	Sample 3 *Bovine dyed crust leather with organic tanning for automotive*	Sample 4 *Sheep not dyed crust leather with organic tanning for leather goods*
Humidity and volatile substances (%)	EN ISO 4684	8,1	8,0	5,4	8,8
Mineral substances (%)	EN ISO 4047	5,1	1,1	1,6	2,5
Organic substances (%)	Residual substances at 102°C- 800°C	86,8	90,9	93,0	88,7
Determination of matter soluble in dichloro-methane (%)	EN ISO 4048	4,4	4,8	7,9	8,5
Determination of the pH of the aqueous extract	EN ISO 4045	3,70	4,80	5,10	3,70
Chemical determination of the Al content (mg/kg)	EN ISO 17072-2	1261	102	755	233
Chemical determination of the Cr content (mg/kg)	EN ISO 17072-2	31822	173	626	57
Chemical determination of the Fe content (mg/kg)	EN ISO 17072-2	286	52	122	123
Chemical determination of the Ti content (mg/kg)	EN ISO 17072-2	25	7	130	43
Chemical determination of the Zr content (mg/kg)	EN ISO 17072-2	-	-	-	5
Sum of tanning metals (mg/kg)	-	33394	334	1633	461

From the values found it is possible to gather that the dyed crust sample tanned with new generation tanning (sample 3), cannot be defined as "metal-free" considering that the sum of the tanning metals, equal to 1633 mg/kg, exceeds the value foreseen by the current standard (1000 mg/kg). Therefore, the adequate definition, from the European Standard point of view, is leather with organic tanning. In fact, in this case the sum of the tanning metals must be equal to or less than 0.3% (3000 mg/kg).

The other two not-chrome-tanned leathers examined (samples 2 and 4) show values of the total content of tanning metals less than 0.1% (1000 mg/kg). Therefore, in this case, leathers obtained with adopted tanning systems can be defined as "metal free".

3.2 VOC results

Figures 1, 2, 3 and 4 show the chromatograms obtained with the GC-MS Purge & Trap technique.

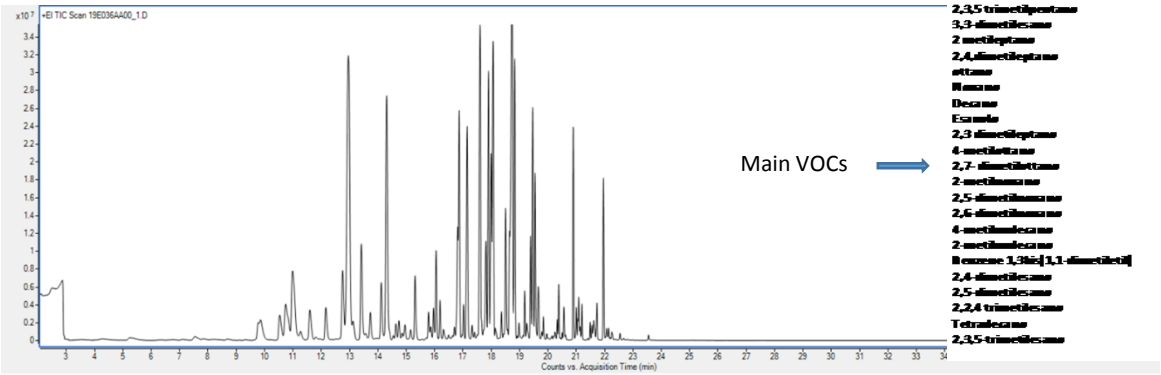

Fig. 1. Chromatographic profile of sample 1.

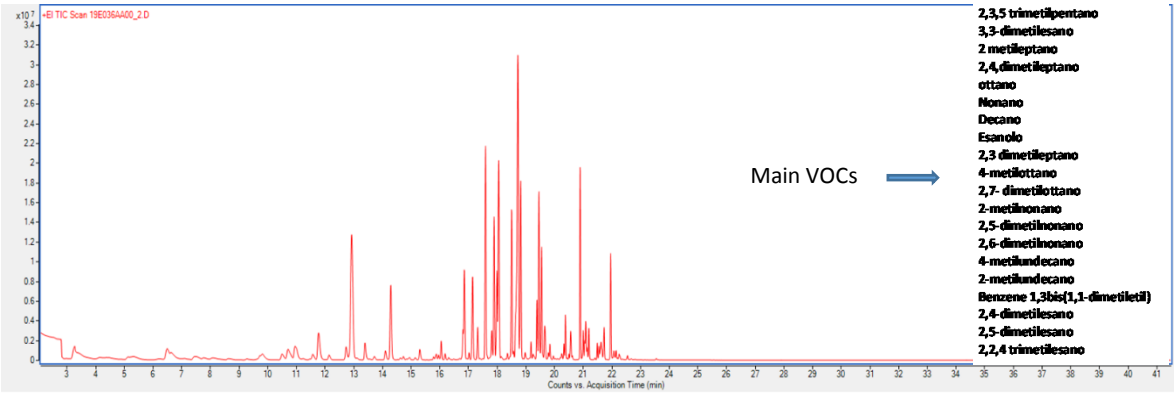

Fig. 2. Chromatographic profile of sample 2.

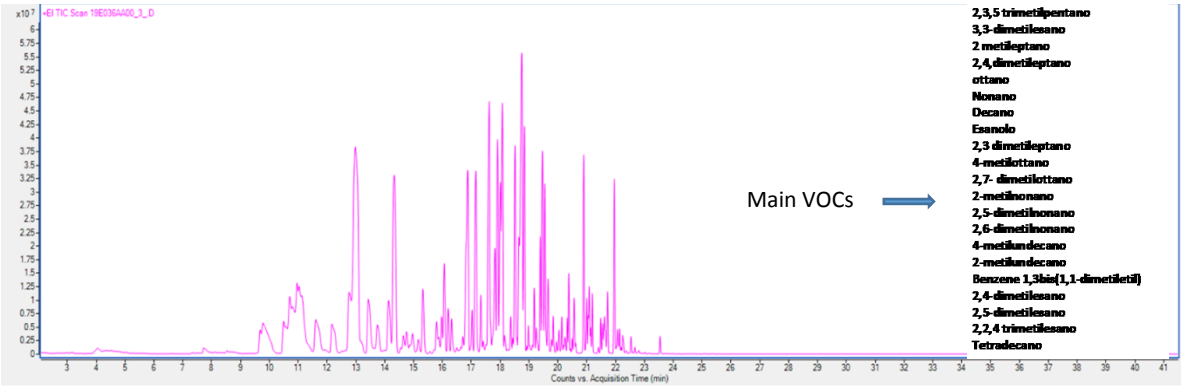

Fig. 3. Chromatographic profile of sample 3.

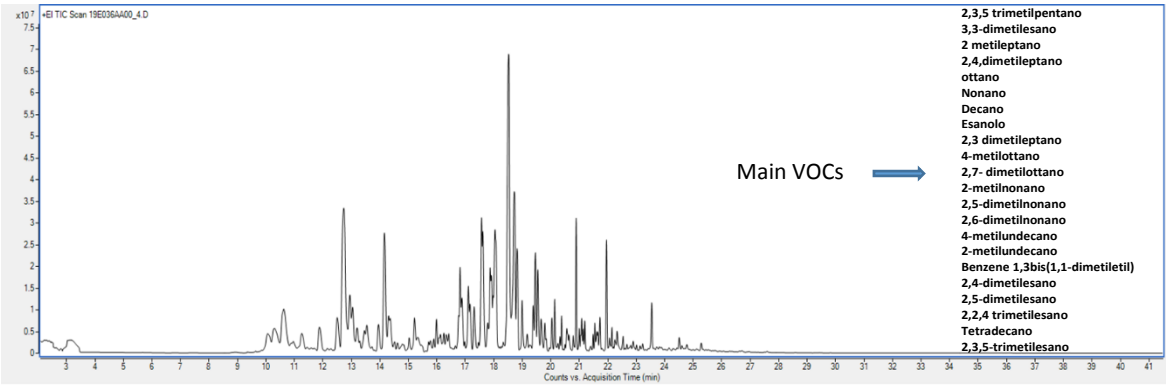

Fig. 4. Chromatographic profile of sample 4.

The results obtained can be summarized as follows:

Sample 1: The chrome leather crust shows the presence of volatile substances hydrocarbons based; in particular, the main constituents concern saturated aliphatic hydrocarbons such as 2,4 dimethyl heptane (CAS 2213-23-2) whose peak, retention time 12,959 minutes, has a higher% area (10.37%). The other families of volatile compounds that have an area greater than 1% are aldehydes (hexanal, Tr = 13413 min., A = 2.20%) and terpenes consisting predominantly of limonene (Tr = 18512, A = 1,93%).

Sample 2: Even the wet-white leather has predominantly VOCs made up mostly of alkanes such as 3.7 dimethyldecane whose peak, retention time = 18.720 min., Presents a higher% area (12.11%). The limonene, in this case, is present with an area% equal to about 4%. Unlike chrome leather, the presence of some aromatic hydrocarbons has also been found (eg toluene, Tr = 11773 min., A = 1.69%).

Sample 3: Bovine leather with new generation organic tanning agents similarly shows the preponderant presence of saturated hydrocarbons; the main component, in terms of area%, turns out to be, as in the previous case, 3.7 dimethyldecane (A% = 5.91). Terpenes such as limonene (A% = 2.61), aldehydes such as the hexanal (A% = 1.73) and long chain alcohols and 2.2 dimethyloctanol (A% = 1.25, Tr = 18650 min., CAS: 2370-14-1), are also present in a significant way. There are also traces of furans.

Sample 4: Finally, sheep's leather with new generation organic tanning agents as well as exhibiting volatile organic compounds such as alkanes of 2,4 dimethylheptane (A% = 7.12, Tr = 12732), aldehydes and limonene (A% = 9.37), it has peaks attributable to halogenated alkanes (eg 2-bromo dodecane, A% = 2.23, Tr = 18821). Also present aromatic hydrocarbons (eg para, ortho, meta xylene, 1,3-di.tert-butylbenzene).

4 Conclusion

The characterization of the leathers examined allowed to appropriately define the terminology of the type of tanning used; for example, according to the EN 15987 standard, metal-free leather must have a total content of tanning metals of less than or equal to 1000 mg/kg (0.1%), while that with organic tanning must not exceed 3000 mg/kg (0.3 %).

Concerning the characterization of Volatile Organic Compounds (VOCs), the analytical investigations have allowed to identify prevalently for all the samples examined the main families of compounds such as, for example, saturated hydrocarbons, aldehydes like the hexanal, terpenes like limonene. Aromatic hydrocarbons are sometimes present, in terms of A%, less significantly than in other families. In the case of sheep's leather with new generation organic tanning agents, the presence of halogenated hydrocarbons has also been highlighted.

Considering that the leathers examined are not finished it is possible to hypothesize that the families of volatile organic compounds identified with the Purge and Trap technique coupled with

GC-MS come from the fatliquiring phase. Future developments of the work may include the determination of VOCs after appropriate tests of artificial aging, for samples processed with different types of tanning.

References

1. *B. Naviglio, M. Tomaselli, D. Naviglio, C. Raia, Caratterizzazione gas-cromatografica delle componenti volatili di pelli e cuoi, CPMC Anno 78 – n.2 marzo/aprile 2002*
2. *M. Tomaselli, B. Naviglio, D. Naviglio, G. Comite, G. Calvanese, XXVIII IULTCS Congress-Firenze, March, 9-12 2005 The characterization of volatile organic compounds in leather,*
3. *M. Tomaselli, B. Naviglio, G. Calvanese, G. Comite, D. Caracciolo, Identification of volatile compounds in the vegetable tanned leather, II Eurocongrss IULTCS, Istanbul, 24-27 Maggio 2006*
4. *Naviglio B., Calvanese G., Cipollaro L., Pierri G., Caratterizzazione di prodotti chimici conciari: ingrassanti, CPMC, 81(4), 231 (2005)*
5. *Naviglio B., Calvanese G., Caracciolo D., Florio C., Romagnuolo M., L'odore del cuoio come parametro di qualità funzionale ed ecologica, CPMC, 87, (4), 163-169 (2011)*
6. *M.Schropfer, M. Czerny, H. Schultz, P. Schieberle, The Odor of Leather, JALCA, 108, 94-107, 2013*
7. *R.M. Cuadros, A. Marsal, L.Ollè, A. Bacardit, J.Font, Characterization of the volatile organic componds by Hs-SPME-GC-MS in the leather sector, JALCA,108, 420-427, 2013*
8. *E. Chorier, N. Blanc,J.C. Cannot, A. Berthod, Headspace GC-MS for thr determination of Halogenated Hydrocarbons, Ethers and Aromatic volatiles in fabric and leather, Jalca, 109, 322-329, 2014*