

Analytical characterization of the not-polar fraction of fats in the course of the leather process

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Abstract: One of the critical points for the classification and the landfill disposal of sludge from leather industry is the determination and the quantification of particular hydrocarbons (C₁₀-C₄₀ fraction), also identified as “Mineral Oils”.

These oils comprise a very large range of hydrocarbon-like by-products of petroleum distillation, labelled in the EU with risk phrase R45 (may cause cancer). According to Italian Legislation on classification of wastes, the threshold limit of mineral oils in not hazardous wastes is equal to 1.000 mg/kg.

The presence of hydrocarbons C₁₀-C₄₀ in the sludge from leather industry can derive from the use of synthetic fatliquors, of various types of waxes but also from the skin itself.

The aim of this work, therefore, is to determine the presence of such hydrocarbons in the leather (raw, limed, wet blue, etc) in the course of the leather process and so to estimate the contribution of such components in the sludge deriving from tannery wastewaters treatment.

The applied methodology previews the solvent extraction of the fats and clean-up of the extract on Florisil. The eluate (not-polar fraction) is analysed both by gravimetric and by GC-MS way.

The preliminary analytical results show that single hydrocarbons or alkanes (docosane, pentacosane, squalene, etc.) with a chain length of more than 10 carbon atoms chain are already present in a raw sheepskin. Although these substances don't give carcinogenic effects, they can be included in the parameter “mineral oils”, so making problematic the classification and the final disposal of the wastes from the leather industry.

Key words: Mineral Oils; hydrocarbons; wastewaters treatment; leather industry

Introduction

The chemical composition of the total fat matter in leather is generally reported in bibliography. Otherwise, few data are available about qualitative and quantitative composition of the not-polar fraction of fats in leather, all along the tanning process.

The knowledge of such substances, generally identified as “Mineral Oils”, can be useful also from the environmental point of view, as their concentration have an impact on the risk classification and the

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disposal of solid and liquid wastes. In fact these oils comprise a very large range of hydrocarbon-like by-products of petroleum distillation, labelled in the EU with risk phrase R45 (may cause cancer). According to Italian Legislation on classification of wastes, the threshold limit of mineral oils in not hazardous wastes is equal to 1.000 mg/kg.

For these reasons and with the aim to evaluate the composition of the main components of not-polar fraction of fats, in this work a characterization on leathers deriving from different phases of tanning process has been carried out by the use of gas chromatographic technique joined to mass spectroscopy (GC-MS). The same investigation also involved the sludges of central wastewaters treatment plant.

Experimental

The determination of mineral oils has been carried out both by gravimetric and by GC-MS way, on the extract deriving from methylene chloride extraction of fats according to ISO 4048, followed by FLORISIL clean-up according to EPA Method 3620C.

The applied methodology previews the solvent extraction of the fats and clean-up of the extract on Florisil. After gravimetric determination and recovery by hexane, the residue (not-polar fraction) is introduced, by cool-on-column injector, into GC column (Restek Rtx-5ms, 5% diphenyl and 95% dimethyl polysiloxane, 0.25 mm ID, 30 meter), then the separated compounds are analyzed by a Quadrupole Mass Selective Detector (HP 5973).

The methodology has been applied on raw, limed, pickled, wet-blue and finished sheepskins provided by a tannery of the Solofra district. As a reference, the GC-MS analysis has been carried out also on a sludge deriving from central tannery wastewaters treatment.

Results

In table 1 the analytical results of the determinations of matter soluble in dichloromethane and of not-polar component are reported.

Table 1 Gravimetric determination of Mineral Oils

	Raw		Limed		Pickled		Wet-blue		Finished	
Volatile matter at 102 °C	41,1%	0,0%	69,7%	0,0%	44,1%	0,0%	62,8%	0,0%	9,1%	0,0%
Matter soluble in dichloromethane	3,0%	5,1%	1,7%	5,5%	2,0%	3,6%	0,5%	1,3%	12,5%	13,7%
Mineral Oils	0,03%	0,05%	0,02%	0,06%	0,03%	0,05%	0,04%	0,1%	1,4%	1,5%

The data evidence that already in the raw sheepskins the mineral oil is present (500 mg/kg) but its

concentration increases very much in the finished leather (15.000 mg/kg), due to the fatliquoring and to the use of waxes in finishing.

According to these results, the solid wastes deriving from wet-blue and finished sheepskins should be classified as hazardous with risk phrase R45.

The following GC-MS determinations have been useful to investigate about the nature of these components. In fact the mineral oils, determined by gravimetric method and therefore in non-specific way, result mainly constituted by hydrocarbons with chain having more than 10 carbon atoms, as it can be seen from Figures 1, 2 and 3. These hydrocarbons are also the main components of not polar fraction of the tannery sludges (see Fig.4) but, in spite of the general risk classification of the Mineral Oils, they, considered one once, are not such hazardous to give carcinogenic characteristic to the waste.

The GC-MS analysis identified other organic substances that are directly correlating with their use in leather processing. Benzoalkanes, deriving from surfactants and finishing additives, are present in all the samples, except for raw sheepskin; the o-hydroxybiphenyl (o-phenylphenol, OPP), used as preservative in the beamhouse operations, is present only in the limed sheepskin; only in the finished leather, the butylated hydroxytoluene (BHT) is found, due to the use as additive for fatliquoring and finishing chemicals.

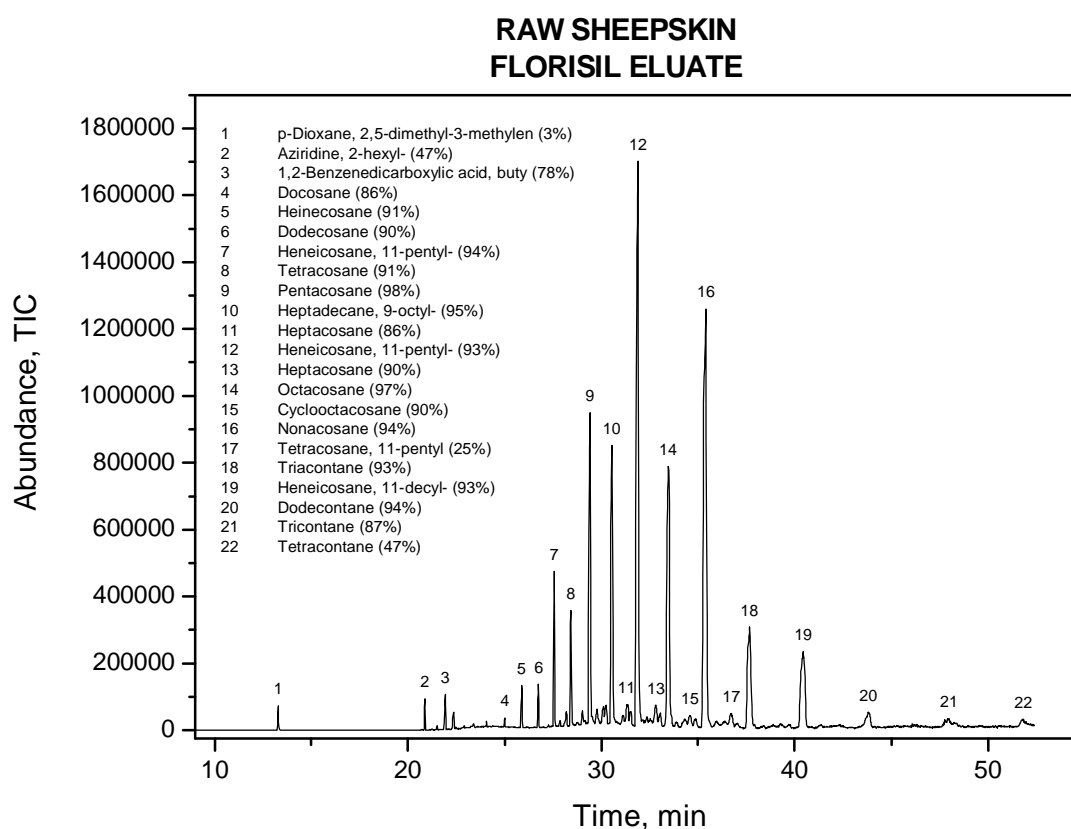


Fig. 1 GC-MS Chromatogram – components of the not-polar fraction of a raw sheepskin

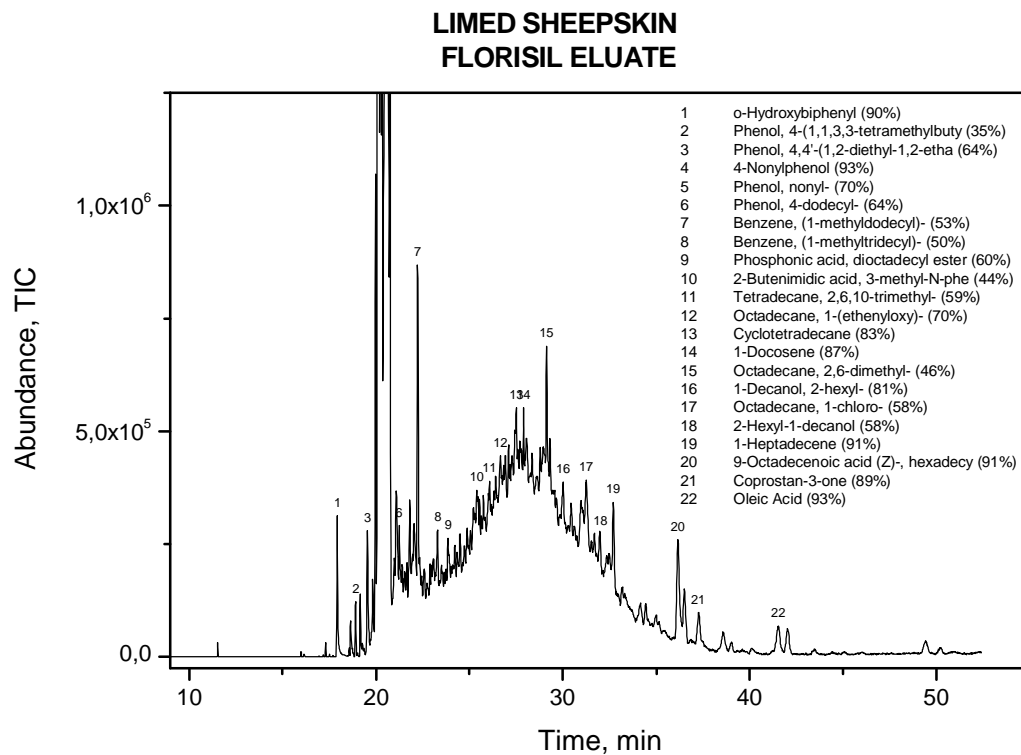


Fig. 2 GC-MS Chromatogram – components of the not-polar fraction of a limed sheepskin

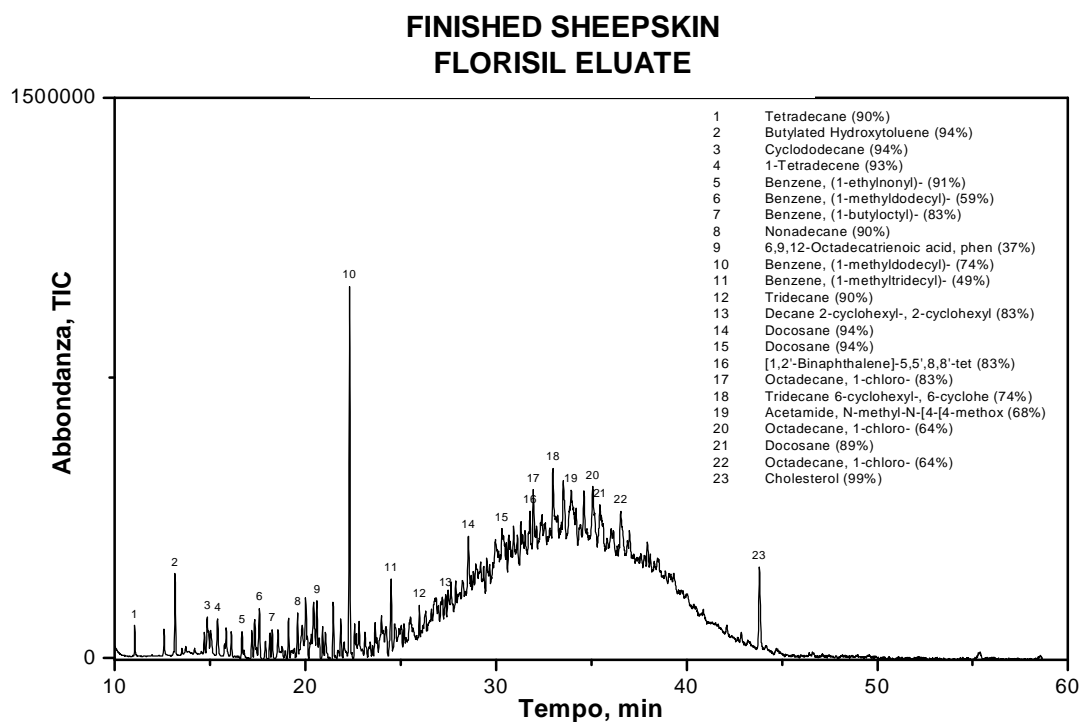


Fig. 3 GC-MS Chromatogram – components of the not-polar fraction of a finished sheepskin

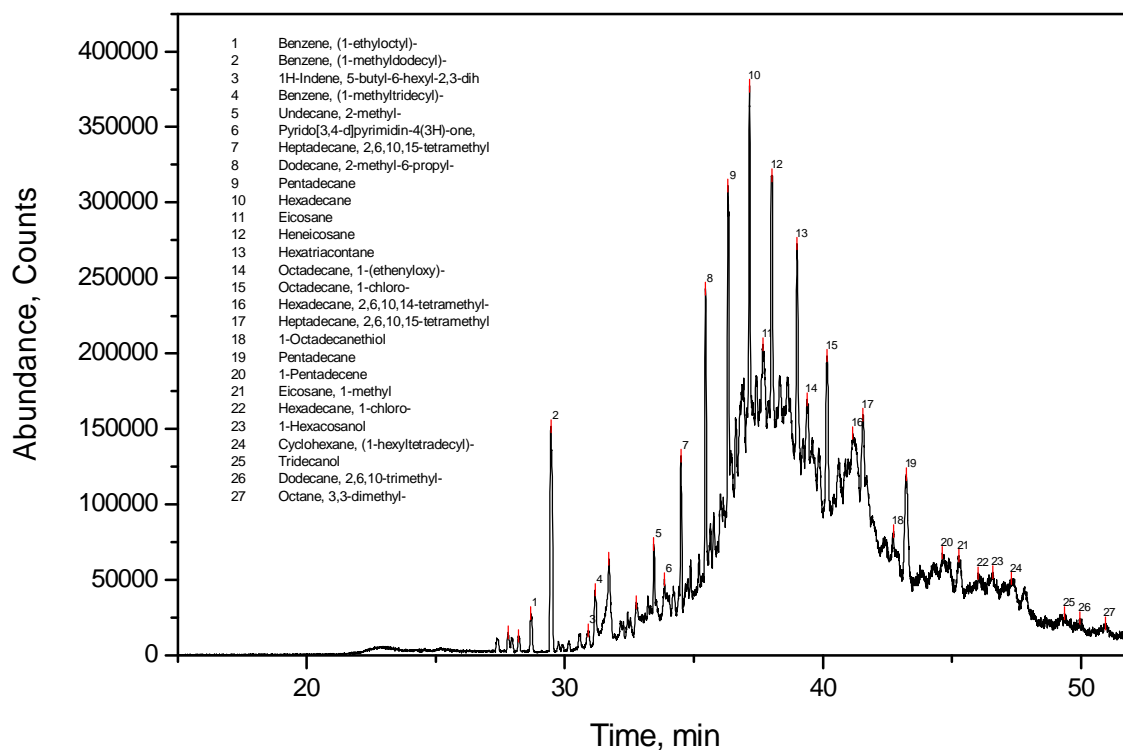


Fig. 4 GC-MS Chromatogram – components of the not-polar fraction of a sludge of the central wastewaters treatment plant

Conclusions

Generally the high content of total fats in the tannery sludge involves also a not negligible amount of “Mineral Oils”, that represents, from the analytic point of view, the not-polar fraction of the fats, analyzed by gravimetric way after Florisil clean-up.

Due to the general risk classification of Mineral Oils as possible carcinogenic, the overcoming of the concentration limit of 1.000 mg/kg make problematic the correct management of tannery wastes, as some control agencies classifies them as hazardous.

The analytic characterisation by GC-MS technique has pointed out that in the leathers, during their processing, the “mineral oils” are constituted by hydrocarbons with high molecular weight, that are also present in tannery sludge. These compounds, some of natural origin, are not dangerous and their characteristics don’t make hazardous the tannery wastes.

References

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