# Determination of the VOCs by Headspace Methods in Leather Production Process

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**Abstract:** In this study, the components which will cause emissions in the old tanning industry were determined, and the processes as potential polluting were shown. Twenty sheepskins from a facility of meat and meat products located in Izmir were processed with a typical clothing sheepskin recipe. Samples were taken from certain production steps and analysed according to Headspace-GC/FID/MS and GC-FID-MS for the volatile organic compounds. This study also evaluated the production steps which will cause emission problems.
**Key words:** leather; headspace; VOC

## 1 Introduction

Volatile organic compounds (VOC) represent an inhomogeneous substance category; its numerous substances cause various impacts. They are responsible for the increase in ground-level ozone concentrations during sunny summer periods and also for the formation of secondary organic aerosols[1]. Furthermore, they contribute to the depletion of stratospheric ozone and to the enforcement of the greenhouse effect. Some components have a carcinogenic, teratogenic or mutagenic character[2]. A number of regulations, e.g. various directives of the European Commission, are in force or currently prepared to limit as well the emissions of VOCs as the concentration of secondary pollutants, for example ozone.

Volatile organic compounds (VOC) are components which, are at room temperature, may be released from materials or products of gases. Classification is conducted according to boiling points in compliance with the Who definition. Compounds boiling from 50°C to 260°C are called VOC: Solvents, residual monomers, plasticizers, fire-proofing agents, processing aids, and preservatives (biocides) reaction and decomposition products are responsible for the occurrence of these emissions. In addition, many health problems are caused particles such as fungi, moulds, bacteria and other microorganisms[3].

Leather tanning is the process of the converting raw hides and skins into leather. Therefore, leather tanning is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. There are several potential sources of air emissions in the leather tanning and finishing industry. Emissions of VOC may occur during finishing processes, if organic solvents are used, and during other processes, such as fatliqouring and drying. Ammonia emissions may occur during some of the wet processing steps, such as deliming and unharing or during drying if ammonia is used to aid dye penetration during dyeing. Emissions of sulphides may occur during liming/unhairing and subsequent processes[4]. Compared to emissions to water, air emissions occur generally in relatively small quantities. Traditionally tanneries have been associated with odour rather than any other air emissions, although the emissions of organic solvents are a major problem. The main emissions to the environment in general arise from odour, organic solvents (VOCs) and total particulate, though emission limits values are also set for ammonia and sulphides[5].

Analysis of volatile on solid matrices is a common analytic problem[6]. The process of identifying the organic compounds present in the 'headspace' or air above the material is termed 'headspace analysis. Both static (closed container) and flow-through or dynamic headspace analyses are used[3]. Headspace gas chromatography combines sampling in a headspace of a closed container, for example, the space

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occupied by gases or vapour in a sample vial, with analysis of the sampled gases or vapour by gas chromatography. The advantage of the headspace sampling is that direct liquid or solid probing is avoided and complex sample matrix in a liquid or solid sample can be simplified or even eliminated in its vapour phase. Traditional static HSGC relies on the vapour-liquid equilibrium (VLE) of a volatile species in a non-volatile matrix within a closed container for determining the concentration of the volatile species in the sample [7].

In this study, volatile organic compounds (VOCs) in the leather samples obtained from different process steps in leather making were analysed by Headspace-GC-FID-MS and distillation-GC-FID-MS.

## 2 Experimental

### *2.1 Material*

In this study, 20 fresh sheepskins were processed according to a typical clothing leather recipe. Leather samples to be used in headspace – gas chromatography- mass spectrophotometer (HS-GC-MS) were taken from the neck, butt and tail areas of the skins at the end of main process steps (soak to finish).

### *2.2 Method*

***For HS-GC-FID-MS***

Leather samples were analysed in an auto-sampler as the following:

Pressure: 20 psi pressure Temperature: 80°C for 15 minutes then increased to 140°C in 3 minutes for injection. Dedector temperature: 230°C; Injection temperature: 200°C (at the Turkish Scientific and Technical Researches Institution - Marmara Research Centre (TÜBİTAK-MAM)).

VOC analysis were realized in Fisons GC-MC (GC 8000 – MD 800)

Column: DB-5, 60 m X 0, 25 mm ID X 0, 25µm film thickness

Pressure: 20 psi

Oven Programme: 30°C for 10 minutes, 10°C/minute to 220°C for 5 minutes waiting

***For Distillation-GC-FID-MS***

Samples taken was distilled in soxhlet apparatus for 6 hours after be ground. Then samples obtained from distillation were injected to HP 6890 Plus GC/5973 – MSD as following programme:
Column: HP-5MS % 5 Phenyl Methyl Siloxane, 30m x 0,25 mm ID x 0,25 µm Film Thickness-HP19091S-433; Column Temperature: 70ºC-3ºC/minute – 250ºC (40 minutes); Carrier Gas: Helium, 1,0 ml/dakika (constant); Split Mod: 1/60; Injection amount: 0,5µl; Liner: Split/Splitless liner (HP-5183-4647)Injection Block Temperature: 250ºC; Auxiliary Temperature: 280ºC; Mass Range:30-350; MS Source: 230ºC; MS Quadrupole:150ºC; Foreline: 67mTorr

## 3 Results and discussion

According to the HS-GC-FID-MS, volatile organic acids (i.e., formic acid, isobutanoic acid, butyric acid, hexanoic acid), alcohols (isobutyl alcohol, 1-chloro 2-butanol, 2, 3-epoxyhexanol and aromatic hydrocarbons (benzene cyclohexenyl, 3-metoxy pentan, methyl terbutylether) were determined in raw sheepskins (Fig. 1). After soaking, formic acid, benzene cyclohexenyl, 1-chlor 2-butanol and butyric acid were determined in samples (Fig. 2). In limed pelts, benzene cyclohexenyl, silane, carbonchloridic acid propyl ester, tetachloro 4-methyl pentene and sulphur were found. Here, sulphur was characteristic compound for the liming (Fig. 3). It can be see volatile organics obtained from deliming process in Fig. 5. In this step formic acid, 2-butanol, benzene cyclohexenyl, 1-kloro 2-butanol and acetic acid were determined. Chromatogram of bating process was given in Fig. 7. Aromatic hydrocarbon (benzene cyclohexenyl), alcohol (1-chlor 2-butanol) and alkane of C6 (cyclohexane) were obtained in bated pelts. Ethanamine, 1, 1-difluoropropene, carbonochloridic acid propyl ester and also an undifened volatile were found in degreased pelts (Fig. 8). In wet-blue leathers, only two volatiles were determined. These were an aromatic hydrocarbon (benzene cyclohexenyl) and an aliphatic alcohol (1-chloro 2-butanol as shown in Fig. 9. And after wet-end processes or retanning, dyeing and fatliqouring, carbonochloridic acid propyl ester and bencen cyclohexenyl were determined in leathers.

In finishing operations, it was used two finish techniques: Water-based and solvent based. 2-propanol (1-metoxy), hexanal, ethanol (2-butoxy) as volatiles and butyl glycol acetat as semi volatile were determined finished leathers (water-based). On solvent-based ones, 2-propanol (1-metoxy), hexanal and ethanol were found as shown Fig. 9 and Fig. 10.

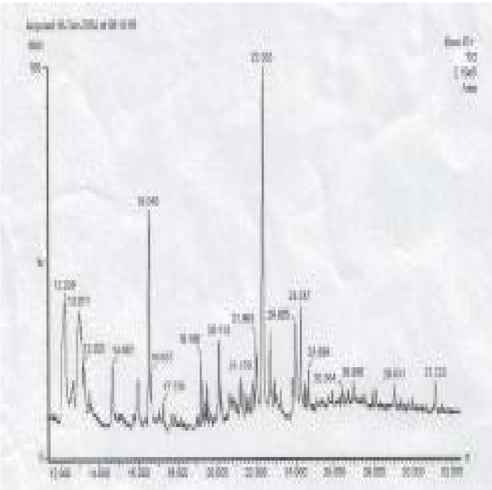

**Fig. 1 VOCs in raw skins**

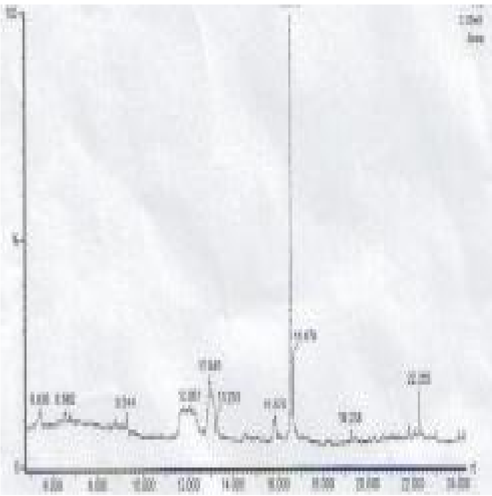

**Fig. 2 VOCs in soaked skins**

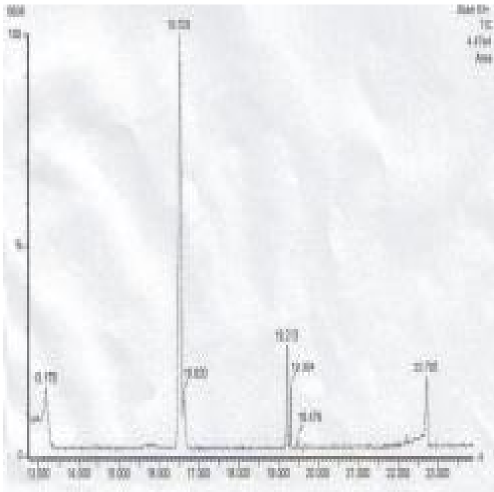

**Fig. 3 VOCs in limed pelts**

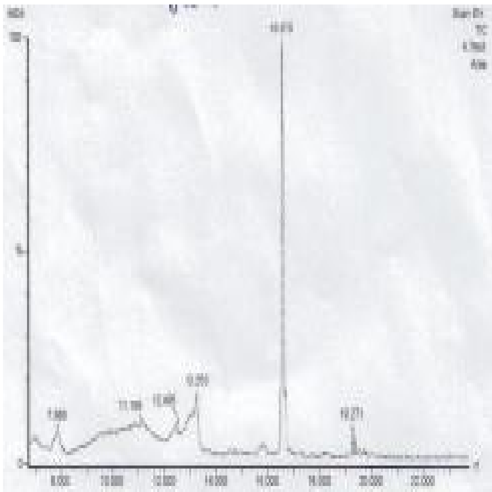

**Fig. 4 VOCs in delimed pelts**

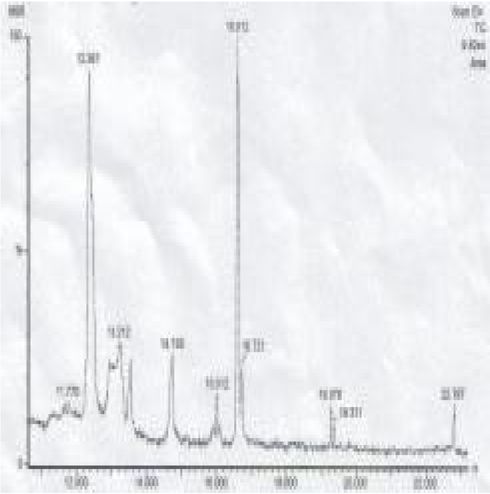

**Fig. 5 VOCs in bated pelts**

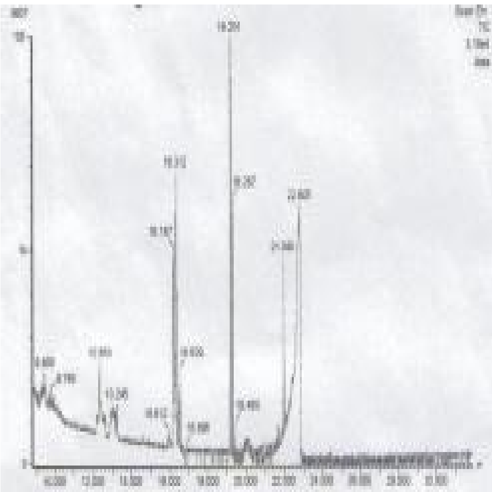

**Fig. 6 VOCs in degreased pelts**

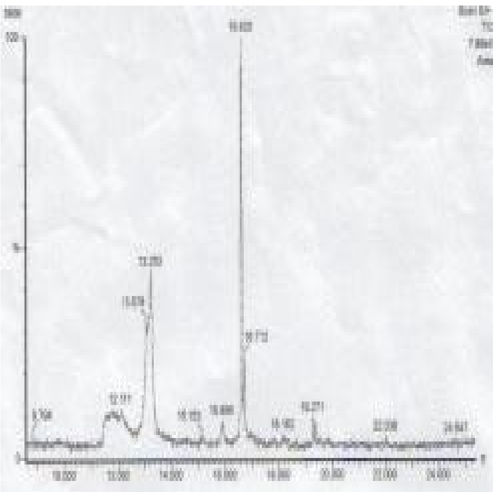

**Fig. 7 VOCs in wet-blue skins**

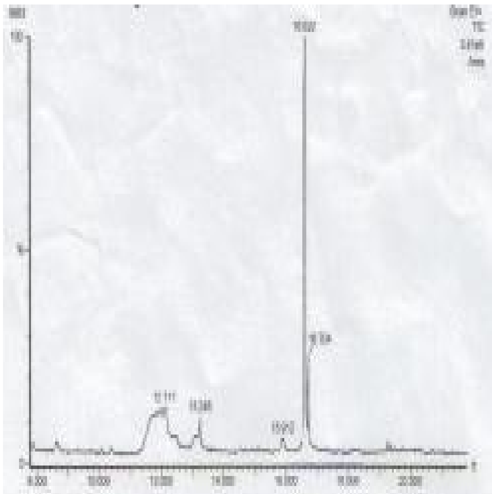

**Fig. 8 VOCs in leather after wet-end**

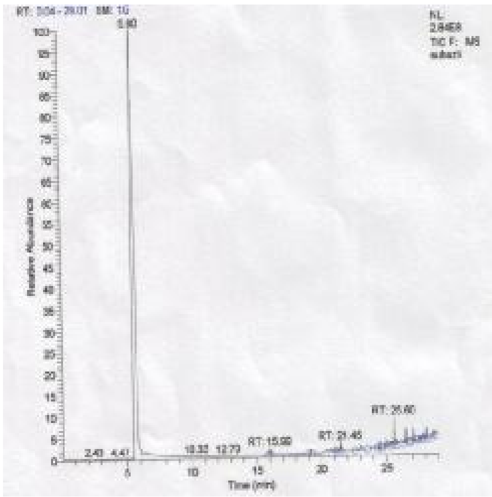


**Fig. 9 VOCs in finished leather (water-based)**

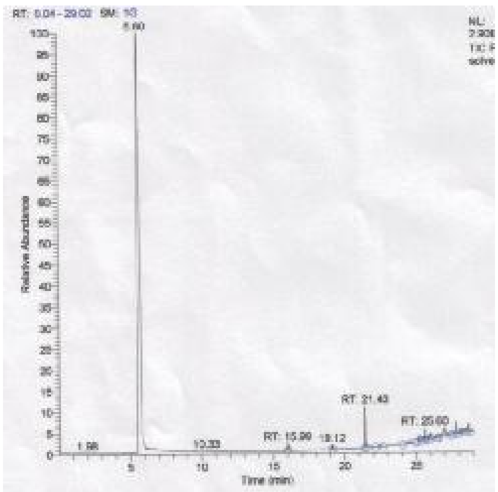


**Fig. 10 VOCs in finished leather (solvent-based)**

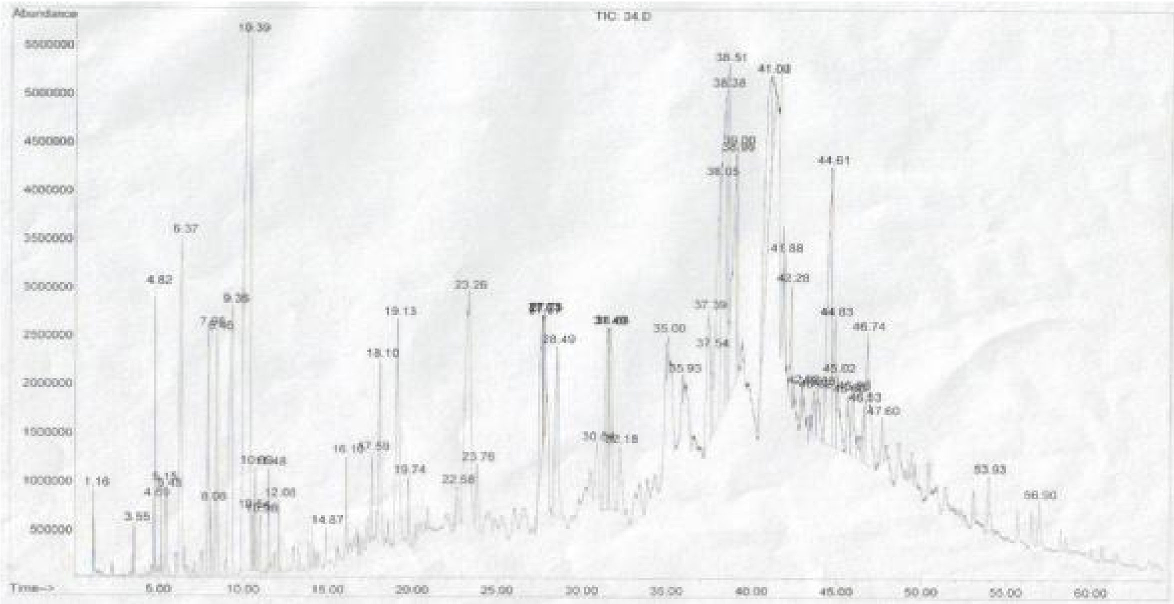

**Fig. 11 GC-FID-MS Chromatogram of finished clothing sheepskin leathers (solvent-based)**

Fifty-two volatiles were determined in the clothing sheepskin leathers applied solvent-based finishing. Half of the volatiles listed as VOC in different environmental institutions. Some of them were aldehydes (for example octanal, nonanal, decanal, undecanal), others were alcohols, glycols, glycoesthers, ketones, aromatic and aliphatic hydrocarbons, volatile organic acids and a semi volatile.

## 4 Conclusions

Data obtained from analyses shows different results. The most important problem here is the way of being obtained analytes. It is real that we need more sensitive preparation techniques and also more detail studies to be able to analyse the leathers for VOCs.

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