

# CHARACTERIZATION OF COMMERCIALY AVAILABLE LEATHERS USING THERMOGRAVIMETRIC ANALYSIS AND PY/GC-MS SYSTEM

by

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## ABSTRACT

The aim of this study is to use the results obtained from the pyrolysis of different commercially available leathers (using thermogravimetric analysis and a pyroprobe device) in order to obtain information about their composition, characteristics and origin. A very small amount of sample is needed to perform these experiments. The results of this work are highly promising, indicating that some specific characteristics of the samples are easily deduced from the pyrolytic results. The results indicate that phenols are related to vegetable tanning and ketones, alkanes and alkenes are related to chrome tanning. The multivariate analysis carried out allows us to distinguish the chromium tanned bovine hides and the chromium tanned goatskin among six different samples (various tanning agents and different origins). The analysis distinguishes the organic tanning from the chrome one regardless of the origin of the leather.

## RESUMEN

El objetivo de este estudio es utilizar los resultados obtenidos a partir de la pirólisis de diferentes cueros disponibles comercialmente (usando análisis termogravimétrico y un dispositivo pirolítico) con el fin de obtener información acerca de su composición, características y origen. Una cantidad muy pequeña de muestra es necesaria para llevar a cabo estos experimentos. Los resultados de este trabajo son muy prometedores, lo que indica que algunas de las características específicas de las muestras se deducen fácilmente de los resultados pirolíticos. Los resultados indican que los fenoles están relacionados con el curtido vegetal y las cetonas, alcanos y alquenos están relacionados con el curtido al cromo. El análisis multivariado realizado nos permite distinguir la piel bovina curtida al cromo de la piel de cabra curtida al cromo entre seis muestras diferentes (distintos agentes de curtido y orígenes diferentes). El análisis distingue el curtido orgánico del curtido al cromo, independientemente del origen del cuero.

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## INTRODUCTION

The reputation of the leather industry over the centuries could be described as one of tolerated usefulness, with a wonderful end product. As the industry enters the 21st Century, it is now recognized as a major industry of great economic importance on an international scale. The raw material of the leather industry is based on the premise of turning the food industry's waste product into a desirable, useful and sustainable range of end products.<sup>1</sup> According to the United Nations Food and Agriculture Organization (FAO), the world production of bovine hides in 2010 was 8115 thousand tons, of which 3146 thousand tons were produced in America, 2654 thousand tons in Asia, 1140 thousand tons in Europe, 883 thousand tons in Africa and the rest in Oceania. The global goatskin production in 2010 amounted to 1129 thousand tons (Asia, Africa, America, Europe and Oceania, with an output of 851, 223, 24, 22 and 8 thousand tons respectively) and sheepskin produced globally (sum of woolled and unwoolled skins) was 2448 thousand tons (the main producer was Asia with 1382 thousand tons followed by Europe with 409 thousand tons, Oceania with 393 thousand tons, Africa with 267 thousand tons and America with 105 thousand tons).<sup>2</sup>

The most obvious differences between goatskin and bovine hides lie in their thickness, weight and surface area. As bovine hides come from larger animals, they have greater thickness, weight and surface area than goatskin. But, apart from this, goatskin and bovine hides present other differences in their dermis structure. In goatskin the grain layer accounts for more than half the total thickness of the dermis, while in adult bovine hides the reticular layer is the largest one. Furthermore, in goatskin the bundles of collagen fibers in the grain layer are very compact causing the grain to be very hard and wear resistant. However, adult bovine hides have a more open skin structure. In the case of bovine hides obtained from younger animals, the structural differences with respect to goatskin are minimized, since the reticular layer is not fully developed and the grain layer is less loose. The origin of the animal is specified in the requirements established by the current legislation relative to the labeling of leather products. Although there is no global legislation about this issue, in some countries like USA (16 C.F.R., Section 24) and some EU countries, like France (Decree n°2010-29) or Spain, (RD 769/1984) there are national regulations for the labeling of leather goods, clothes, furniture and other products.

Nowadays, the identification of the animal origin of leather is commonly carried out by means of visual observation with microscopy, since chemical analyses imply many difficulties. The typical characteristics observed in leather are the porous structure of the surface and the cross-section, in order to find the physical differences explained above. This method requires a great experience and skilled operators. It cannot be

considered a rigorous and conclusive method since this is a task which is fraught with serious difficulties. For example, the porous structure cannot be seen if the leather has been treated with pigments, has been sanded or it is a split leather. A similar case happens if it is a dark skin. One can also be easily wrong in the identification of the leather when it has undergone a treatment that crushes the surface fibers or in cases where the skin thickness is low. In about 50% of the cases leather cannot be identified properly by visual observation with microscopy.

On the other hand, the chemical analysis usually carried out for animal origin determination consists of DNA sequencing of skins and hides.<sup>3</sup> The genome sequence of many domestic and farm animals, like cows, pigs, goats, sheep, horses, chickens, cats and dogs are available now, but the scarcity of laboratories capable of doing it and the cost of this kind of tests are the main disadvantages of this analytical method. Besides, DNA sequencing is not suitable for leather because the tanning process removes the genetic material. For this reason it would be interesting to find an easier chemical method to distinguish among different animal origins of leather. In relation to the tanning agent, since its introduction by Knapp in 1858, chrome tanning has gradually replaced vegetable tanning and now 90% of leather worldwide is produced by chrome tanning.<sup>4</sup> Fixing the tanning agent to the protein of the leather may occur as a result of one of the following mechanisms of interaction according to the type of tanning agent used:<sup>5</sup> covalent bonds (aldehyde, oxazolidine or methacrylic polymer tanning), coordinate covalent bonds (inorganic or mineral tanning) or hydrogen bonds and dipolar bonds (vegetable extract tanning).<sup>6</sup> The efficiency of the tanning process is usually measured by the shrinkage temperature method (IUP16), the stronger the bonds the higher the shrinkage temperature. However, this test requires a large amount of sample which in some cases poses a big problem. An alternative method is differential scanning calorimetry (DSC), which is used mainly to evaluate the deterioration of parchments or historical leathers, being less common in other leather sectors.<sup>7-9</sup> In this context it could be interesting to provide a simple method to characterize different samples (in terms of origin or tanning agent used). Pyrolysis is the thermal decomposition of a material in an inert atmosphere. Different devices and types of reactors can be used to perform this type of experiments. For example, thermogravimetric analysis has been widely used in many fields of material decomposition research. The earliest research in thermogravimetry dates back to the 1950's and 1960's, when scientists such as Madorsky, Chatterjee, Conrad, Kilzer and Broido studied the high temperature degradation behavior of cellulose.<sup>10-12</sup>

On other hand, the use of a Pyroprobe device connected on-line to a gas chromatograph/mass spectrometer (Py/GC-MS) allows a rapid analysis of the pyrolytic products

generated in the process to be obtained. These products are related to the structure of the pyrolyzed sample. The advantage of using this technique is that it allows a rapid screening of the chemical composition of a sample at a molecular level. Both techniques had been previously used by our research group to study the viability of using pyrolysis as a method to characterize bovine leather with different tanning treatments<sup>6</sup> as well as the NaOH treatment of these samples,<sup>13</sup> together with other devices such as a vertical lab scale reactor<sup>14</sup> to study the pyrolysis of different samples of bovine leather.

After verifying the validity of the Py/GC-MS for the characterization of tanning agents in bovine leather, we tried to apply this method to hides and skins of different origin and tanned with different tanning agents. An added difficulty has to be taken into account when working with commercially available leather since different finishes can be found from one sample to another. In order to analyze all the information obtained from the pyrolysis experiments in an objective way, a multivariate analysis has been used. This mathematical method has been applied to different research fields, such as the pyrolysis of agricultural residues,<sup>15</sup> environmental studies of water, soil or air quality<sup>16-19</sup> or studies related to food technology<sup>20-21</sup> and many others. The objective of this paper is to check the viability of using the results from thermogravimetric analyses and Pyroprobe pyrolysis runs (for which only some milligrams of sample are needed) to characterize commercially available leathers, their origin, the tanning agent and type of finish used in an objective way.

## MATERIALS AND EXPERIMENTAL EQUIPMENT

### Materials

The experiments were carried out with bovine hides and goatskin tanned with three different tanning agents (chromium, vegetable tannins and glutaraldehyde). These are commercially available leathers provided by Spanish tanners; randomly selected and representative of those used for common uses such as footwear, leather goods or upholstery. No more information about these samples was firstly inquired.

### Elemental Microanalyzer

An elemental CHNS microanalyzer provided with a LECO's TruSpec microdetection system was used. This equipment uses a combination of a continuous flow of helium as the carrier gas, an infrared detector and a thermal conductivity detector.

### Thermobalance

The thermogravimetric analysis was carried out in a TGA/SDTA 851 Mettler-Toledo thermobalance. The temperature of the sample was measured using an R type thermocouple. The temperature values used were those recorded by the probe of the device, located under the crucible, and not the programmed values.

### Pyroprobe

For the flash pyrolysis of the samples a Pyroprobe 2000 (CDS Analytical Inc.) was used. The sample was put in the center of a cylindrical quartz capillary (38 mm L, 3 mm I.D.). The capillary was automatically placed in the center of a platinum coil heated under an inert atmosphere. The analysis of pyrolysis vapors in the condensable gas range was carried out using a gas chromatograph (HP-6890N Agilent Technologies) with a capillary column HP-5MS, provided with a mass spectrometry detector (HP-6973 inert MSD Agilent Technologies) for the analysis.

## EXPERIMENTAL PROCEDURE

### Ultimate Analysis

The technique is based on the complete and instantaneous oxidation of the sample by combustion with pure oxygen at a temperature of about 1000 °C. The different combustion products CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>, are transported by the carrier gas (He) through a reduction tube and then selectively separated into specific columns to be thermally desorbed. Finally, the gases pass separately through a thermal conductivity detector that provides a signal proportional to the concentration of each of the individual components of the mixture.

### Thermobalance

The temperature range selected for the thermogravimetric study was 25-800°C with a nominal heating rate of 10°C min<sup>-1</sup>. The analysis was carried out in a nitrogen atmosphere with a flow rate of 50 ml min<sup>-1</sup>. The amount of sample analyzed was around 8 mg, taken as two cylindrical portions of 2 mm diameter. The leathers were approximately 2 mm thick.

At the start of the study the equipment was calibrated using indium and aluminum standards; later periodic checks were carried out to ensure that the equipment met the calibration specifications.

### Pyroprobe 2000

A Pyroprobe 2000 was connected online to a gas chromatograph-mass spectrometer (Py/GC-MS). The parameters used in this process were: nominal heating rate: 20°C/ms; pyrolysis time: 20 s; process temperature: 500°C. Each experiment was repeated twice, and the results proved the reproducibility of the experiments.

The products generated by the pyrolysis were rapidly removed from the reaction zone using a helium flow through a transfer line at 280°C until they were put into the GC-MS equipped with a capillary column HP-5MS for analysis. The qualitative analysis of the program obtained was carried out using the commercial mass spectra libraries WYLEY275 and NIST02. More details about the experimental equipment can be found elsewhere<sup>6</sup>.

### Multivariate Analysis

The IBM SPSS 19.0 for Windows software was used in this study for data analysis and evaluation. The principal component analysis (PCA) was applied to analyze the interrelationships among a large number of variables (in our case the selected compounds). First, the factor matrix containing the correlation between each variable and the factor was calculated. The first factor or principal component provides the best summary of linear relationships among data. The second factor is defined as the second best linear combination of variables, subject to the orthogonality of the first. The remaining factors are defined analogously. Not rotated solutions achieve the goal of data reduction but usually do not offer an adequate interpretation of the variables examined. Thus rotation of factors is made, which involves rotating the reference axis origin of the factors to achieve a simpler factor pattern. The Varimax method is the most widely orthogonal rotation method used. This method keeps angles of 90 degrees between the reference axes and minimizes the number of variables that have high loadings on each factor. A cluster analysis was also performed. This technique aims to generate groups (called clusters) with observations (each sample), in such a way that within the groups the most homogeneous observations are joined and these groups are the most heterogeneous possible.

## RESULTS AND DISCUSSION

### Ultimate Analysis

Table I shows the elemental analysis of these materials. The vegetable tanning resulted in an increased amount of C and lower N and S content. Bovine samples treated with glutaraldehyde or chromium showed a high percentage of N.

### Thermobalance

Each test was repeated three times in different days to check the reproducibility of the test, which was found to be acceptable as the difference in measurements was less than 1°C.

Thermogravimetric curves (TG) as well as derivate weight loss curves (DTG) of the samples tested are shown in Figure 1. Significant differences in the decomposition temperature range as well as in the shape of the curves can be easily detected. Thus for example, vegetable and glutaraldehyde tanning processes produce sharp peaks while using chromium as a tanning agent leads to wider peaks. By comparing the samples of different origin (bovine and goat) it can be observed that goat's DTG curves show a defined shoulder regardless of the tanning agent used, which indicates different decomposition steps. The moisture content can be estimated from the degradation step at around 100°C. This value is around 9-11 %. All the samples showed a residue value higher than 22 % (23 % in dry basis), especially the vegetable tanned bovine leather that showed a 33% (35 % in dry basis) residue value.

Table II shows the temperature average values at which the maximum decomposition rate takes place as well as the average percentage of the residue generated in dry basis. The standard deviation of these values has also been included. From the values shown in this table, it can be deduced that, in general, tanned bovine hides generate a higher amount of solid residue than their goat equivalents. According to the results obtained, chromium tanned leathers clearly increased the temperature of the maximum decomposition rate by approx. 20°C with respect to the other samples. The low value reached by the vegetable tanned bovine leather sample has to be noticed. This low temperature is not observed in the cases of other vegetable tanned leathers or other bovine samples. A more rigorous search of information about the vegetable tanned bovine leather indicated that this sample corresponded to leather intended for footwear soles that contained a higher percentage of vegetable tanning agents than other hides or skins. This fact could explain the sharp decrease in the temperature of the maximum decomposition rate and the large percentage of solid residue obtained in the thermogravimetric analysis.

**TABLE I**  
**Elemental Analysis of Materials (% dry weight)**

		CHROMIUM		VEGETABLE		GLUTARALDEHYDE	
		BOVINE	GOAT	BOVINE	GOAT	BOVINE	GOAT
Elemental analysis	N	11.3	9.8	8.7	8.2	13.4	10.8
	C	41.3	42.9	46.7	49.4	43.8	44.9
	H	6.05	6.36	6.10	6.66	6.63	6.54
	S	2.01	1.79	1.05	0.91	0.94	1.97
Moisture		14.5	11.4	11.5	10.6	11.7	10.2

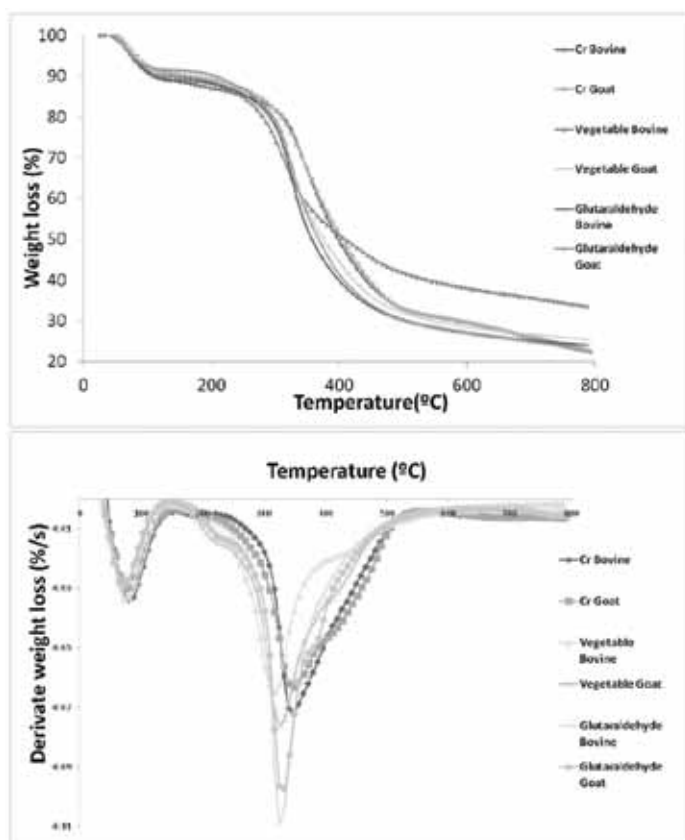


Figure 1. TG and DTG of the samples.

**TABLE II**  
**Temperature of Maximum Decomposition Rate and Solid Residue Obtained in the Thermogravimetric Analysis.**

Origin	Tannage	Max. decomposition T <sup>a</sup>	%* Solid residue <sup>a</sup>
Bovine	Chromium	342.0 ± 1.3	24.3 ± 0.8
Goat	Chromium	343.0 ± 1.6	24.0 ± 0.7
Bovine	Vegetable	311.6 ± 0.8	35.3 ± 1.4
Goat	Vegetable	323.2 ± 0.5	27.3 ± 0.4
Bovine	Glutaraldehyde	322.7 ± 0.9	26.1 ± 1.0
Goat	Glutaraldehyde	326.4 ± 0.3	23.4 ± 1.1

<sup>a</sup>average value ± SD; \*In dry basis

### Pyroprobe

The pyrolytic behavior of the samples studied was also compared using a Py/GC-MS system. The reproducibility of the results was checked by repeating each run twice and the results obtained were compared. Figure 2 shows two experiments performed using the same sample (Chromium tanned bovine leather) and the same equipment under the same conditions on different days. From these results, it can be deduced that for compounds with a percentage area higher

than 15%, the error calculated as  $(X_i - X_m)/X_m$  (where  $X_i$  is the yield obtained in run  $i$  and  $X_m$  is the average value) is smaller than 5%. In the case of compounds with percentage areas in the range 15 - 5%, the error is below 14%. For smaller percentage areas, the estimated error increases.

Figure 3 shows the pyrograms corresponding to the samples studied in this paper. This figure reflects the complexity of the pyrograms. As can be noted, the pyrolytic products detected vary depending on the tanning agent and the origin of leather. From Figure 3, it can be deduced that the glutaraldehyde tanning agent tends to equalize the pyrolytic volatile composition regardless of the origin of the leather, while the chromium tanning agent shows the differences as a function of the sample origin.

For data processing, chromatographic peaks with a relative area higher than 1%, in at least one of the samples, were selected and identified. The addition of these selected compounds reached around 74-84% of the total chromatogram (depending on the sample). Table III shows a list of these compounds and their average values of relative areas in the pyrograms analyzed. Most of the compounds detected correspond to nitrogen derivatives, generated from the leather proteins. For an easier analysis of results, the compounds were grouped according to their functional group. Table IV shows the percentage of total quantified peak area, classified according to functional groups, for each sample. By analyzing the different tanning agents, it was found that chrome tanning generated a lower proportion of heterocyclic aromatic compounds and a higher percentage of ketones, alkanes and alkenes, compared with vegetable tanning and glutaraldehyde. By comparing their origin, goatskin produced a lower proportion of nitriles and heterocyclic aromatic compounds and a higher proportion of alcohols, alkanes and alkenes compared to bovine leather. In previous studies carried out by our research group working with differently tanned bovine leathers, some characteristic pyrolysis products were associated to specific tanning agents. This is the case of phenols, which are produced in a higher percentage in the pyrolysis of organic tanned samples, especially with the vegetable tanning agent<sup>6</sup>. However, in this paper, the results showed a higher increase in the percentage of phenols in the pyrolysis of commercial samples tanned with glutaraldehyde than with vegetable tanning. In order to check these data, the test of tannins and phenols with gelatin and ferric chloride was conducted on the glutaraldehyde tanned sample, reaching a positive result. This fact could be the consequence of having subjected the sample to a retanning process with tannins, which obviously would increase their presence and thus, the generation of phenols in the pyrolysis process. In this sense, it is logical to think that the greater similarity between both chromatograms of glutaraldehyde tanned samples is due to the double tanning process that tends to equalize the pyrolytic volatiles obtained shadowing the footprint of the original identity.

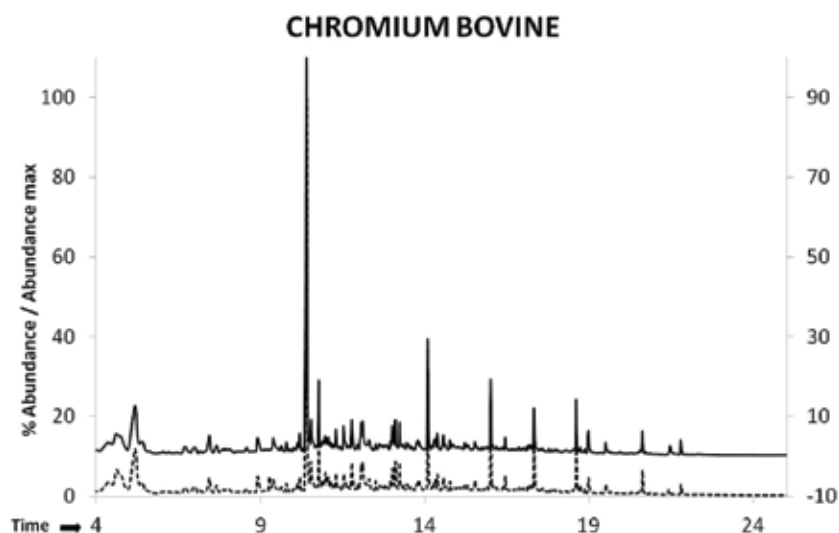


Figure 2. GC-MS chromatograms of the chromium tanned bovine sample obtained on different days represented as the relative abundance.

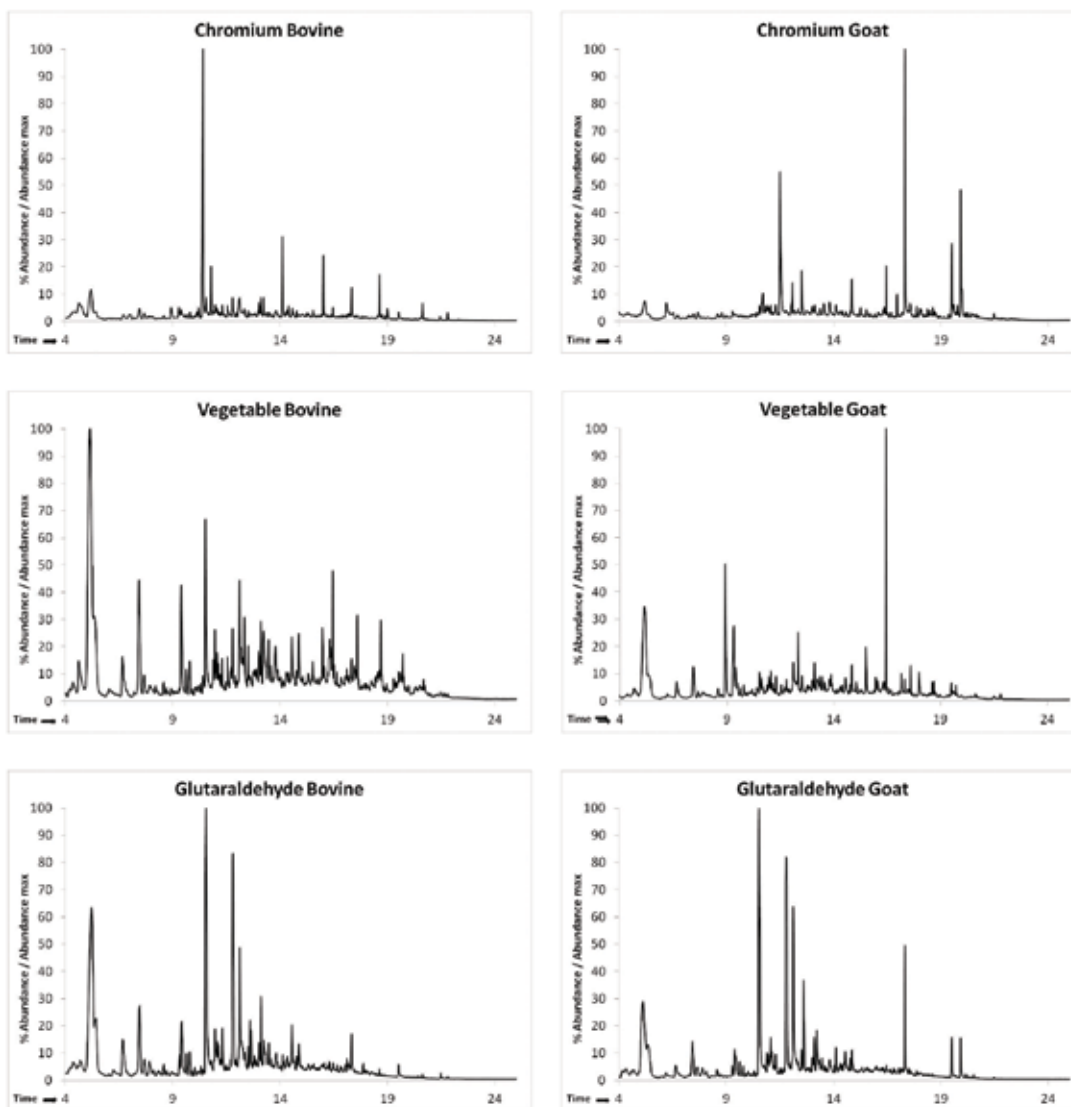


Figure 3. GC-MS chromatograms of chromium, vegetable and glutaraldehyde tanned bovine and goat samples represented as % of abundance for the maximum abundance.

**TABLE III**  
**Average Percentage of Total Quantified Peak**  
**Area of Identified Compounds.**

Peak #	TANNAGE	CHROMIUM		VEGETABLE		GLUTARALDEHYDE	
	LEATHER ORIGIN	BOVINE	GOAT	BOVINE	GOAT	BOVINE	GOAT
1	Pentane,1-nitro (d)	2.790	0.694	1.165	0.607	1.258	1.038
2	Pyridine (b)	7.403	0.127	3.158	1.673	1.303	0.830
3	1H-Pyrole (b)	9.320	4.277	27.247	18.533	20.973	12.423
4	Toluene (c)	1.566	0.757	5.740	4.304	4.843	4.586
5	N-Hexanal (a)	0.000	3.219	0.000	0.324	0.000	0.000
6	2-butenoic acid (c)	0.000	1.002	0.000	0.000	0.000	0.000
7	1H-Pyrole, 1-ethyl- (b)	0.762	0.512	0.676	1.915	2.790	0.741
8	1H-Pyrole, 3-methyl- (c)	1.677	0.716	5.087	2.933	3.896	2.714
9	Ethanol, 2-butoxy- (c)	1.480	0.312	0.000	9.105	0.129	0.000
10	2,4-Pentanediol, 2-methyl- (c)	1.407	0.466	0.090	4.701	0.619	0.423
11	1H-Pyrole, 2,5-dimethyl- (d)	1.655	0.104	3.563	2.224	2.841	1.152
12	Benzenamine (b)	23.745	0.295	0.451	0.331	0.000	0.000
13	Phenol (a)	2.684	0.000	4.699	1.305	12.841	15.963
14	Hexanoic acid (d)	0.780	2.562	0.142	0.379	0.000	0.205
15	3-Pyridinamine (d)	1.372	0.000	0.000	0.000	0.000	0.000
16	3-Ethyl-4-methylpyrrole (c)	0.000	0.000	0.000	1.115	1.151	0.579
17	2-butanol (d)	0.000	1.010	0.000	0.000	0.000	0.000
18	1H-Pyrole, 2-ethyl-4-methyl- (b)	0.828	0.000	1.347	0.000	1.041	0.000
19	2-propanol 1-(2-methoxypropoxy) (d)	0.000	0.882	0.000	1.099	0.000	1.031
20	Benzenemethanamine (b)	1.217	1.069	0.513	0.774	1.201	0.630
21	2-Pyrrolidione, 1-methyl- (b)	1.137	13.823	0.157	0.562	0.000	0.000
22	Phenol 2-methyl- (a)	1.445	0.000	1.606	0.000	8.563	15.705
23	2-pentyl-4-methylsazole (d)	0.885	1.778	3.025	0.245	0.186	0.362
24	Phenol 3-methyl- (a)	1.718	0.000	1.171	1.686	3.476	5.892
25	1H-Pyrole, 2,5-dimethyl- (c)	0.000	0.000	0.000	0.000	1.303	0.838
26	Phenol 2-methoxy (guaiacol) (a)	0.000	0.000	1.467	2.574	0.584	0.000
27	Nonanal (b)	0.000	2.844	0.784	0.813	0.577	0.000
28	Phenol 2,6-dimethyl (a)	0.197	0.000	0.000	0.000	1.082	3.576
29	Cyclopentanone, 2,2-dimethyl- (d)	1.350	0.763	0.783	0.694	0.845	0.547
30	Benzeneacetonitrile (a)	1.556	0.839	1.089	1.154	1.632	1.034
31	4-acetylpyridine (d)	0.000	0.000	2.222	1.274	0.644	1.748
32	Octanoic acid (d)	0.156	1.071	0.000	1.274	0.000	0.000
33	2-piperidinone (d)	0.000	0.000	1.022	0.332	0.000	0.000
34	1-dodecene (a)	0.000	1.537	0.000	0.000	0.000	0.000
35	Unknown*	4.767	0.958	0.000	0.000	0.000	0.000
36	Benzenepropionitrile (b)	0.839	0.000	1.006	0.479	1.310	0.768
37	Nonanoic acid (b)	0.133	2.891	1.340	1.458	0.831	0.903
38	4-vinyl-2-methoxy-phenol (a)	0.000	0.000	0.348	2.043	0.114	0.000
39	2,6-dimethoxyphenol (b)	0.000	0.000	1.084	0.663	0.000	0.000
40	Tricyclo[4.2.0.0(2,4)]oct-7-en-5-one (d)	3.108	0.000	0.000	0.000	0.000	0.125
41	Tetradecane (a)	0.488	2.330	1.555	7.626	0.000	0.000
42	Decanedioic acid, diethyl ester (d)	0.000	1.281	0.167	0.000	0.000	0.191
43	CIS-ISOEUGENOL (a)	0.000	0.000	0.000	1.046	0.000	0.149
44	1-Pentadecene (a)	1.932	15.072	0.477	0.762	0.993	3.547
45	[1,1'-Biphenyl]-2-ol (a)	0.000	0.723	0.093	1.569	0.067	0.101
46	1-Hexadecene (a)	2.409	0.437	0.138	0.383	0.115	0.000
47	Cyclotetradecane (a)	0.453	4.794	0.098	0.019	0.319	1.284
48	Pentaethylene glycol (d)	0.000	1.174	0.000	0.000	0.000	0.000
49	Ethanol 2-(dodecyloxy)- (b)	0.000	7.445	0.000	0.000	0.000	1.175
50	2-Propanol 1-(2-methoxy-1-methylthoxy)- (d)	0.000	1.826	0.000	0.000	0.000	0.000

Identification quality: (a)  $\geq 95\%$ , (b) 90-95%, (c) 80-90%, (d) 50-80%.

\* m/z 69,131,219,262, 326; MW 326

It is worth noting the high percentage of nitrile and amine compound groups produced in the pyrolysis of chrome tanned bovine leather. This increase is mainly due to the high relative value of benzenamine obtained in the pyrolysis of this sample. Benzenamine is a product used in the leather dyeing process<sup>22</sup>. In this case, the commercial chrome tanned bovine leather was dark-colored leather, which justifies the generation of this compound. This example clearly shows the relationship between the pyrolytic products obtained and the characteristics and treatments of the samples.

A multivariate statistical analysis was developed to perform a wider comparative study among the samples. The PCA and the hierarchical cluster were carried out in such a way that the chromatograms were transformed into a matrix with 6 rows and 50 columns (significant compounds identified in Table III). The PCA gave 3 principal components that could account for the 80% of the variance. Table V shows, in individual and cumulative percentages, the total proportion of explained variance for each factor, for both rotated (Varimax rotation) and non rotated solutions. Figure 4a shows the scatter plots from PCA comprising the first two principal compounds obtained from the rotated component matrix. The loading analysis showed that the chromium tanned goatskin was

basically defined by Principal Component 1 while the chromium tanned bovine sample was highly related to Principal Component 2. The Principal Component 1 was defined mainly by the compounds 21, 6, 34, 48, 17, 19, 5, 44, 49, 14, 47, 42, 27 and 37 (many of them contain oxygen in their composition) vs 36, 11, 4, 8 and 3 (heterocyclic aromatic compounds and toluene) in Table III. In the case of the Principal Component 2, it was basically defined by compounds 46, 35, 12, 15, 40, 29, 1 and 2 (ketones and amines mainly) vs 31 and 4 (4-acetylpyridine and toluene) numbered in Table III. According to these results a clear differentiation between chromium tanning and vegetable and glutaraldehyde tanning was observed (it has to be noted that glutaraldehyde tanned samples were subjected again to vegetable tanning).

Furthermore, it could be noted that chromium tanned samples can be differentiated according to their origin. Thus the loading plot allowed us to distinguish between bovine hides and goatskins after being tanned with chromium. The multivariate analysis was repeated without taking benzenamine into account (compound 12, which is the dyeing agent used for chromium tanned leather) to avoid any interference induced by this additional component, and the same result has been obtained. This differentiation of

**TABLE IV**  
**Classification and Area Percentage of Compounds**  
**Identified with Py-GC/MS.**

TANNAGE LEATHER ORIGIN	CHROMIUM		VEGETABLE		GLUTARALDEHYDE	
	BOVINE	GOAT	BOVINE	GOAT	BOVINE	GOAT
Heterocyclic aromatic compounds	22.531	7.514	46.323	29.913	36.127	21.386
Phenols	6.043	1.174	10.375	9.317	26.659	41.283
Aromatics	1.566	0.757	5.740	4.304	4.843	4.586
Nitriles and amines	31.520	2.897	4.222	3.345	5.401	3.470
Acids, esters and aldehydes	1.069	14.870	2.434	4.248	1.408	1.299
Alkanes and alkenes	5.281	24.170	2.268	8.790	1.427	4.831
Ketones	5.595	14.587	1.962	1.588	0.845	0.672
Alcohols	2.887	12.664	0.183	16.473	0.815	2.731

**TABLE V**  
**Total Variance Explained.**

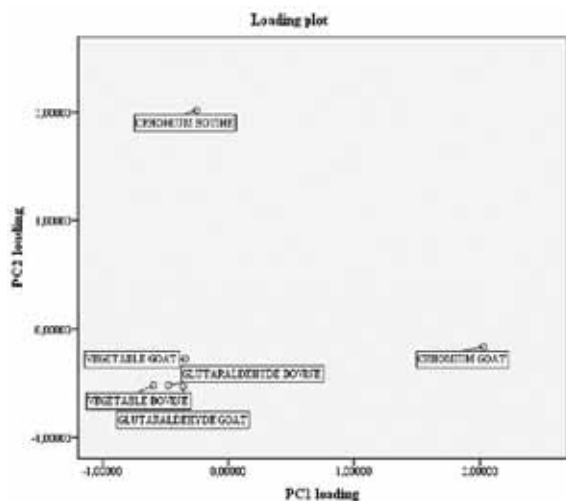
Component	Total variance explained					
	Sums of squared loadings of the extraction			Sum of squared loadings of the rotation		
	Total	variance %	cumulative %	Total	variance %	cumulative %
1	20.181	39.571	39.571	20.061	39.335	39.335
2	11.923	23.378	62.950	10.521	20.629	59.965
3	10.201	20.003	82.952	8.395	16.461	76.425
4	5.450	10.686	93.638	7.904	15.498	91.923
5	3.244	6.362	100.000	4.119	8.077	100.000

Extraction method: Principal Component Analysis

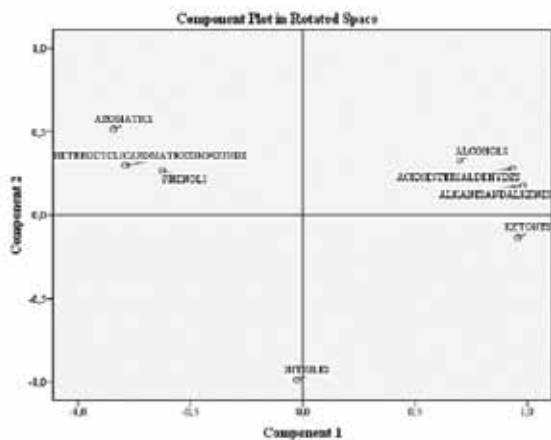
chromium tanned samples according to their origin had been reported previously in view of the chromatograms observed, thus the multivariate analysis showed in an objective way what had been deduced from the visual observation of the chromatograms.

In order to simplify the analysis and add another perspective to the problem, we performed a new statistical study using as variables the groupings according to the chemical functionalities shown in Table IV. Figure 4b shows the component plot and scatter plots of this study. As can be noted, chromium leathers were again set apart from the other four samples. It could also be observed that the variables, with the Varimax rotation, were grouped into the principal components as follows: PC2 was defined basically by nitriles and PC1 was defined by the aromatic or linear character of the compound. A similar analysis was performed by removing the benzenamine compound (dye) from the chromium bovine sample with similar results to those obtained in Figure 4b.

The analysis of the hierarchical clusters standardizing the values for the variables (% area of the compounds) was also carried out, obtaining the dendrogram shown in Figure 5. This study showed a greater similarity between the glutaraldehyde tanned samples of different origin (bovine and goat), which were combined at a lower level in the scale. From this point, subsequent additions of the rest of the samples were observed, being the chromium tanned goatskin the one more clearly separated in the dendrogram. Taking the origin of the samples into account, it could be noted that the chromium tanning process generated different products according to the origin (bovine or goat) (rescaled cluster distance 11); this distance was reduced in the case of vegetable tanning (rescaled distance cluster 4), being minimum in the case of the glutaraldehyde tanning process (rescaled cluster distance 1). This fact confirmed a higher degree of the homogeneity in the pyrolytic products produced by the glutaraldehyde tanned samples.



a) All compounds studied as individual variables



b) Compounds grouped according to functional groups studied

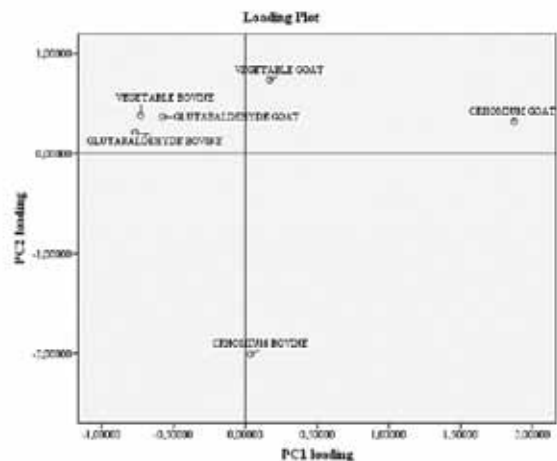


Figure 4. Scatter plots from PCA of leathers of different tannage and origin

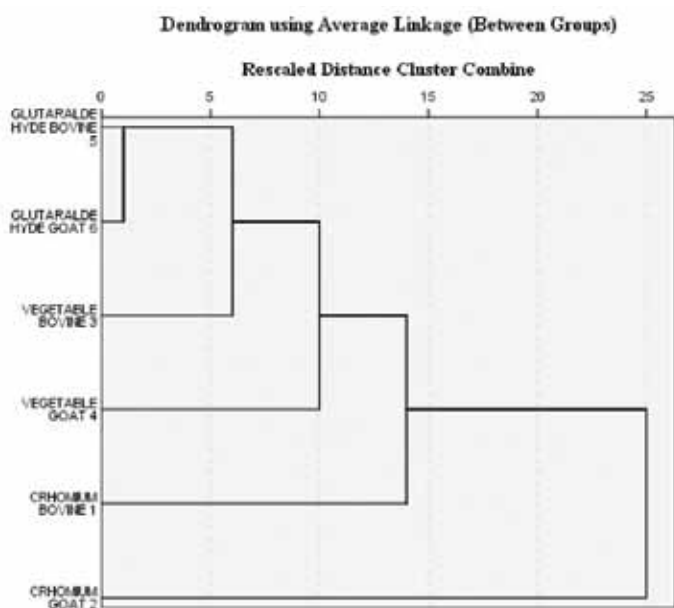


Figure 5. Dendrogram resulting from the hierarchical cluster analysis of the rescaled distance.

## CONCLUSIONS

The application of pyrolysis techniques to the characterization of commercially available leathers provided interesting results. Specific compounds were especially associated to their corresponding samples. Thus, phenols were related to vegetable tanning and ketones, alkanes and alkenes to chrome tanning. By comparing their origin, goatskin produced a higher proportion of alcohols, alkanes and alkenes than bovine leather. Just using a small amount of sample, specific characteristics of the samples such as percentage of tanning agent, eventual inclusion of tannins in the process and inclusion of color agents, among others, could be easily deduced from the thermogravimetric analysis and pyrolytic volatiles generated.

It can be concluded that the multivariate analysis allowed us to classify chromium tanned samples according to the origin distinguishing between bovine or goat samples. Moreover, a second statistical analysis with the groups of compounds classified according to their functionality showed a differentiation between nitrile compounds (PC1) and linear and aromatic compounds (PC2). The organic tanning agents seemed to modify the products generated in the pyrolysis of the samples of different origin to a lower extent. However, the cluster analysis showed a more evident clustering as a function of the origin, which proved that the tanning process masked these similarities, but did not eliminate them. According to the results obtained, the characterization of the skin origin by pyrolytic methods is considered a promising research topic that could result in the development of a standard method to characterize hides and skins in a quick and simple way using a very small amount of sample.

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## REFERENCES

1. International Council of Tanners (<http://www.tannerscouncil.org/perspective.htm>)
2. Food and Agriculture Organization of the United Nations (<http://www.fao.org>)
3. Brabetz, W; Proof of origin for raw hides with biomolecular methods. 4<sup>th</sup> Freiberg Collagen Symposium, 2008.
4. DasGupta, S; Zirconium acetate-oxazolidine combination tannages. *JSLTC* **94**, 167-169, 2010.
5. Gratacos, E., Boleda, J., Portavella, M., Adzet, J.M., Lluch, G; Tecnología Química del Cuero. *Emporium*, Barcelona, 1962.
6. Marcilla, A., García, A.N., León, M, Martínez, P, Bañón, E; Analytical Pyrolysis as a Method to Characterize Tannery Wastes. *I&EC Research* **50**, 8994-9002, 2011.
7. Chahine, C; Changes in hydrothermal stability of leather and parchment with deterioration: a DSC study. *Thermochimica Acta* **365**, 101-110., 2000.
8. Fessas, D., Signorelli, M., Schiraldi, A., Kennedy, C.J., Wess, T.J., Hassel, B., Nielsen, K.; Thermal analysis on parchments I: DSC and TGA combined approach for heat damage assesment. *Thermochimica Acta* **441**, 30-35, 2006.
9. Popescu, C., Budrugaec, P., Wortmann, F.-J., Miu, L., Demco, D.E., Baias, M.; Assessment of collagen-based material which are supports of cultural and historical objects. *Polymer Degradation and Stability* **93**, 976-982, 2008.
10. Madorsky, S.L., Hart, V.E. and Strauss, S.J.; Pyrolysis of Cellulose in a Vacuum. *Journal of Research of the National Bureau of Standards* **56**, 343-358, 1956.
11. Chatterjee, P.K and Conrad, C.M.; Kinetics of the Pyrolysis of Cotton Cellulose. *Textile Research Journal* **36**, 487, 1966.
12. Kilzer, F.J. and Broido, A.; Speculations on the nature of cellulose pyrolysis. *Pyrodynamics* **2**, 151-163, 1965.
13. Marcilla, A., García, A.N., León, M, Martínez, P, Bañón, E; Study of the influence of NaOH treatment on the pyrolysis of different leather tanned using thermogravimetric analysis and Py/GC-MS system. *Journal Analytical and Applied Pyrolysis* **92**, 194-201, 2011
14. Marcilla, A., León, M., García, A.N., Bañón, E., Martínez, P; Pyrolysis of tannery wastes in a fluidized bed reactor (2010) 3rd International Symposium on Energy from Biomass and Waste (VENICE) 978-88-6265-008-3

15. Manyá, J.J., Ruiz, J. and Arauzo, J.; Some peculiarities of conventional pyrolysis of several agricultural residues in a packed bed reactor. *Ind. Eng. Chem. Res.* **46**, 9061-9070, 2007
  16. Pires, J.C.M., Sousa, S.I.V., Pereira, M.C., Alvim-Ferraz, M.C.M., Martins, F.G.; Management of air quality monitoring using principal component and cluster analysis - Part II: CO, NO<sub>2</sub> and O<sub>3</sub>. *Atmospheric Environment* **42**, 1261-1274, 2008
  17. Mandal, U.K., Warrington, D.N., Bhardwaj, A.K., Bar-Tal, A., Kautsky, L., Minz, D., Levy, G.J.; Evaluating impact of irrigation water quality on a calcareous clay soil using principal component analysis. *Geoderma* **144**, 189-197, 2008
  18. Skrbic, B., and Durisic-Mladenovic, N.; Principal component analysis for soil contamination with organochlorine compounds. *Chemosphere* **68**, 2144-2152, 2007
  19. Singh, C.V.; Pattern characteristics of Indian monsoon rainfall using principal component analysis (PCA). *Atmospheric Research*, **79** 317-326, 2006
  20. Brito, G., Andrade, J.M., Havel, J., Díaz, C., García, F.J., Peña-Méndez, E.M.; Classification of some heat-treated liver pastes according to container type, using heavy metals content and manufacturer's data, by principal components analysis and potential curves. *Meat Science* **74**, 296-302, 2006
  21. Silva, B.M., Andrade, P.B., Martins, R.C., Seabra, R.M. and Ferreira, M.A.; Principal component analysis as tool of characterization of quince (*Cydonia oblonga* Miller) jam. *Food Chemistry* **94**, 504-512, 2006
  22. Adzet Adzet, J.M.; Química-Técnica de tenería. 1985.
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