Times are changing…, in the leather chemical laboratories

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1. Introduction

There is a real evolution in the consumer's behavior since 30 years. The times where durability, hard-wearing quality or product performances were priorities, are gone. At the beginning of the XXI century, innocuousness is one of the first priorities for the consumer. Several major crisis such as, "mad cow disease", dimethylfumarate in shoes, lead in toys, have alerted the consumers and the authorities have multiplied the laws everywhere in the world. Looking back to the last 10 years, major changes have occured in the leather sector:

- ✓ Legislation has changed in Europe. Since 2007, REACH was created to protect people from critical substances. This regulation requires the control of a large number of organic/inorganic chemicals.
- ✓ Now, all the companies have a sustainable development policy. Innocuousness, low environmental impact, ecological design, wastes management, etc. are major parameters for the final consumer. The production chemicals control is a priority.
- ✓ Health and safety requirements are changing. All the specialists have noticed that the population is reacting more and more to allergens.

All commercial brands and the big retailers have therefore developed specifications included in their technical files. These requirements define by products or by material the restricted substances. The Tannery is now faced to a wide number of these specifications that have been developed without any coordination between stakeholders (brands, manufacturers, retailers, authorities and consumers association). This situation is critical for the tanners; they still need to control their manufacturing, but they shall be especially able to demonstrate the leather innocuousness.

From a gravimetric or colorimetric chemistry, the routine laboratories have switched to complicated techniques. The consequences are important for the chemistry laboratories of the tannery:

- ✓ People are different, new skills are needed
- ✓ New machines, new laboratories, large investments are necessary
- ✓ New test methods, standardization are strategic
- ✓ New relation between the parties, lobbying are needed.

We would like ant to study this evolution and its consequences.

2. Legislation reminder

Worldwide, the consumers associations request a better protection for the products users; the authorities have implemented new legislation to ensure the innocuousness of the products on the market to avoid the presence of certain chemical substances. Everywhere there is an inflation of new regulation based on the precautionary principle.

In Europe, Regulation N° 1907/2006, concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), especially 2 annexes are very important,

- Annex 14 defines the candidate list for the substances of very high concern "SVHC". If a SVHC is present at a concentration higher than 0.1% in the product, the consumer shall be informed. It is mandatory to answer within 45 days to any customer request.

- Annex 17 gives the list of forbidden substances. This annex includes the former Directive N° 1976/769/ CE and all its amendments (e.g. Aromatic amines coming from azodyes, organotins, etc..)

In the USA, Law 16 CFR 1303 bans lead in certain consumer products, leather articles (footwear, leathergoods, toys…) are concerned. Proposition 65 of the state of California defines also a list with a large numbers of critical substances.

In China, a standard defines the rules :GB 20400-2006, restriction of hazardous substances in leather and fur, setting the content limits of hazardous substances in fur and leather products such as banned Azo dyestuffs and formaldehyde.

Many other countries could be also mentioned, Japan, Republic of Korea, Turkey…Table 1 give a non-exhaustive list of the substances commonly analyzed in leather.

Table 1: Substances frequently analyzed in leather

Substance Group	**purposes**	**Standard for analysis**	leather	Coated leathers (PVC,PU,etc.)
chromium	tanning agent	EN ISO 5398 part 1 to4	x	x
formaldehyde	Pre-tanning, tanning and re-tanning agent, finishing	EN ISO 17226-1 / IUC 27-1	x	x
Biocides (TCMTB, PCMC, OPP, OIT)	protection of hides and skin	EN ISO 13365 / IUC 29	x	x
Total Heavy Metals	dyes, tanning agents	EN ISO17072-2 / IUC27-2	x	x
Soluble Heavy metals	dyes, tanning agents	EN ISO17072-1 /IUC 27-1	x	x
pH	consequence of the tanning process	EN ISO 4045 / IUC11	x	x
Alkyl phenols / Ethoxylates	surfactants	pr EN ISO 18218-1 / IUC 28-1 pr EN ISO 18218-2 / IUC 28-2	x	x
Aromatic amines	AZO colorants	EN ISO 17234-1 / IUC20-1 EN ISO 17234-2 / IUC 20-2	x	x
Chlorinated paraffin's (SCCP C10-C13)	previously in fat liquor	pr EN ISO 18219 / IUC 30	x	x
Chlorophenols (PCP, TeCP,..)	biocides	EN ISO 17070 / IUC 25	x	x
Dimethylformamide	solvent for PU	pr CEN ISO TS 16189		x
Dimethylfumarate	forbidden biocide	CEN ISO TS 16186	x	x
Phthalates	plasticizers	CEN ISO TS 16181		x
Chromium VI	consequence of the tanning process	EN ISO 17075 / IUC 18	x	x
Organotins	biocides	CEN ISO TS 16179	x	x
PFOS	previously in waterproof agent	CEN TS 15968	x	x
Polycyclic aromatic hydrocarbons (PAH's)	degradation of substances, polymers	pr CEN ISO TS 16190		x

These substances are more and more complex and need sophisticated apparatus to be analyzed, let's take an example.

3. Development of Polycyclic aromatic hydrocarbons (PAH's) in Leather

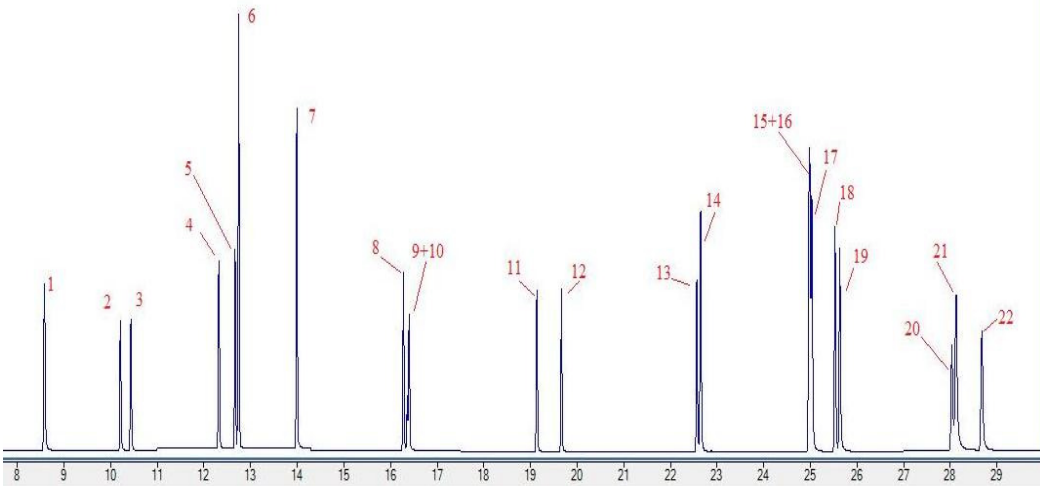
In plastics production, mineral oils are used to re-soften the material. Often these mineral oils can contain PAH as an impurity. PAH may also be included in carbon black used for coloration and filling of plastics and rubber. During the last few years, German consumer protection organizations and authorities have identified high concentrations of PAH in many consumer products, such as toys, shoes or tool grips. This is of concern because some PAH have carcinogenic and mutagenic properties. Germany proposes to include the PAH in the annex XVII of REACh and mentions leather as a material potentially containing PAH.

To be able to apply this regulation CTC has developed a test method in its laboratory using a high technical instrumentation like gas chromatography coupled with tandem mass spectrometry.

The PAH's can be found in polymers, dyeing formulations or as degradation products. The chemical group of PAH's includes more than hundreds of compounds but only a few is monitored. The determination is made according to the standard pr CEN ISO TS 16190. The method is based on ultrasonic extraction with hexane and direct analysis of the extract with GC/MS-MS.

The figure 1 represents a Total Ion Chromatogram of a mixture of PAH's used for calibration.

Figure 1 : Chromatograph for PAH's

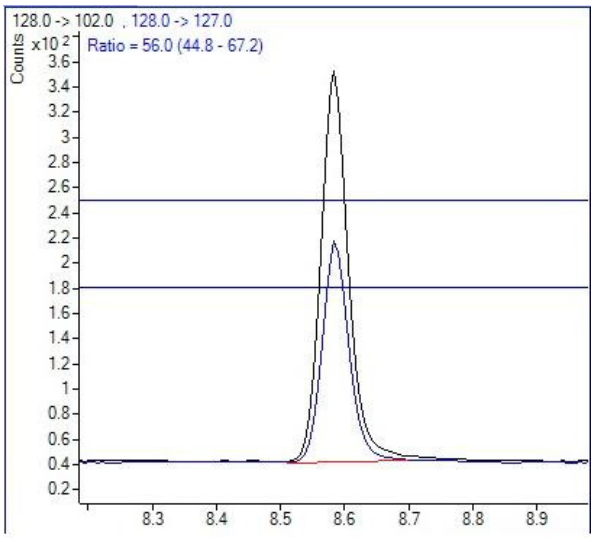


1 Naphthalene	7 Fluorene	13 Benzo(a)anthracene	18 Benzo(e)pyrene
2 2-methyl naphtalene	8 Phenanthrene	14 Chrysene	19 Benzo(a)pyrene
3 1-methyl naphtalene	9 Anthracene-D10	15 Benzo(b)fluoranthene	20 Indeno(1,2,3-cd) pyrene
4 Acenaphtylene	10 Anthracene	16 Benzo(j)fluoranthene	21 Dibenzo(a,h) anthracene
5 Acenaphtene-D10	11 Fluoranthene	17 Benzo(k)fluoranthene	22 Benzo(g,h,i)perylene
6 Acenaphtene	12 Pyrene		

The use of high technical instrumentation, such as triple quadruple mass spectrometer, induces spending time in the optimisation of each compound for the determination of their MRM transitions.

A MRM transition consists of choosing one or two precursors ions and the resulting product ions with the suitable collision energy.

The figure 2shows the two transitions for naphthalene (calibration standard at 10 µg/l).



Primary transition (black line)
128 → 102 (Collision energy : 20 EV)

Secondary transition (blue line)
128 → 127 (Collision energy : 20 EV)

Figure 2 : MRM transition

With legal requirement at the level of mg/kg or µg/kg, the leather analyst needs more precise and accurate methods. At CTC, the test methods are validated with the two standard NF T90-210 and NF T-90-220.

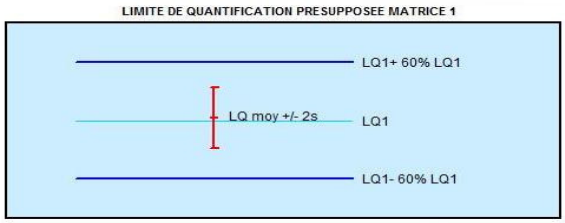
The first standard concerns the dynamic range of the method as well as the limit of quantification (LOQ) and the specificity of the method. The NF T-90-220 deal with uncertainty and the tools used to determine them (spiked samples, interlaboratory trials…).

For the LOQ, two different spiked samples were analysed per day, during five different days. The table 2 and figure 3 show a series of results for spiked samples at the LOQ and their graphic representation.

Table 2 : Results of method validation

Results (LOQ level material 1)			value	10.00
tests	1	2	average	Standard deviation
19/06/2012	10.9	10.21	10.55	0.23
20/06/2012	7.57	7.96	7.77	0.08
21/06/2012	10.93	11.06	10.99	0.08
23/06/2012	9.99	10.34	10.17	0.06
26/03/2012	12.3	11.44	11.87	0.36

Figure 3 : Validation of expected LOQ



4. Discussion

The tanners are under an increasing pressure:

- more advised consumer may pay a key role by asking more detailed information related to hazardous substances in consumer goods,
- retailers technical files including chemical specifications more and more complicated and specific,
- legal authorities increasing the market control.

The tanners shall be sure of the innocuousness of their leather, and the production control is very important. It is therefore essential to be strict with the manufacturing process to avoid any deviation that could cause problems.

The production control shall focus on:

- Human resources:
  the staff shall be trained and controlled. All the people shall be aware of the effect of any deviation to the manufacturing process.
- Process:
  Work sheets shall be available to avoid ill-fated initiative.
  Certain substances mentioned in table 1 are degradation products. This means that they have not been used during the tanning process but they appear due to a wrong step in the process (too high temperature, insufficient rinses,…)
- Machinery:
  All the production tools shall be calibrated and well maintained.
- Consumables:
  The control of the chemicals used in the process is obviously a major parameter. It is essential to be confident with the suppliers and to have a careful selection of them. Several substances of table 1 can be found in leather because they were present in the rough materials. The tanners shall request certificates of conformity and shall oversee what they are buying. The use of old chemicals shall be forbidden.

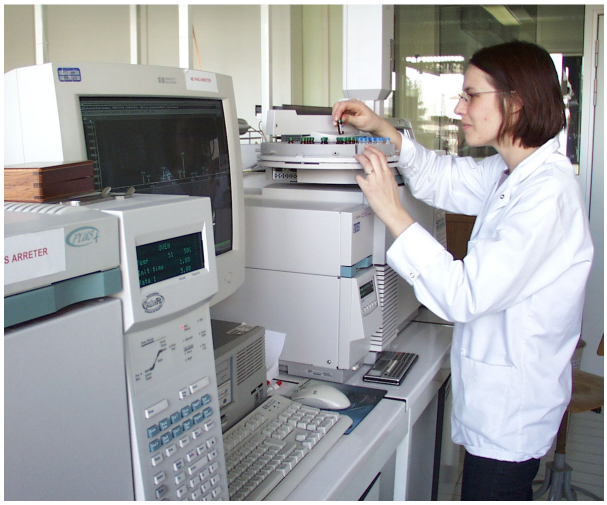
The chemical analysis is essential for the tanners for the rough material but also for the leather itself. As shown in the PAH development example, it is less and less possible for a tannery to have internally the expertise for this complex work, essentially for economic reasons.

- ✓ People are different, new skills are needed.
  Only fully educated staff can work on these new chromatographic technics. This means that it is necessary to recruit engineers in analytical chemistry or higher level of training. But not only, complex samples preparation, apparatus maintenance, require a full team. The laboratory team salary will constitute an important charge.
- ✓ New machines, new laboratories, large investments are necessary. Each substance requires more or less a specific apparatus for aromatic amines, it is needed HPLC-

DAD (50 Keuros) and GC-MS (70 Keuros) - for PAH, it is needed GS-MS-MS (120 Keuros) for heavy metals, ICP-OES (60 Keuros) is necessary.
These example wull give you an idea of the investment, but do not forget that these delicate machines need also a clean and air-conditioned environment. The cost of the consumables (glassware, chemical,) shall also be taken into account.

Therefore the relation between the tanners and the laboratory used for the controls shall be optimal. Controls plans shall be defined. Rough materials, skins, wet blues, and leathers must be statistically surveyed to ensure the manufacturing process with an economical cost acceptable for the tannery.

Figure 4 : The analysis laboratory



The speeding up of the technical progress and the people minds have fully changed the situation. Leather is a complex chemical matrix, leather analysts are still necessary to produce useful information and not only figures. The relation between the tanners and their controls supplier will have to change in order to become a real collaboration between 2 partners.

The social responsibility is more and more mentioned on the leather market. The ISO 26000 standard covers this wide field and innocuousness is for sure one of the major challenge to solve in the next future years.