Development of methods for the analysis of dangerous Sunstances in liquid or solid matrices coming from the leather sector

Dr Nathalie GYURAN - HUMBERT
Dr Jean-Claude CANNOT
Centre Technique Cuir Chaussure Maroquinerie 4 rue Hermann Frenkel 69367 LYON Cedex 07 France

I. INTRODUCTION

The contemporary company is increasingly aware of the importance of the environment, of which it is perceived at the same time dependent and responsible.
From now on, the search for dangerous chemical substances falls under the concept of development durable, reconciling the environmental protection, the innocuisness of the products for the consumer, and the economic development.

The industrialists of the leather sector were confronted with the problems of environmental protection and the lawful constraints are increasingly strict and complete.
Until the beginning of the Nineties, only the basic parameters of waste water (DCO, DBO, pH...) were followed and controlled.
Since then, the situation has developed considerably with requests for monitoring parameters such as PCP (pentachlorophenol), HAP (aromatic hydrocarbons polycyclic) and many other organic micropollutants whose list is steadily increasing. The last stage of this process being the publication of the European directive on the water (2000/60/CE) **[1]** which lays down in particular a Common policy in the field of waste water.

In the same way, there has been a real evolution of the behavior of the consumers for the 10 last years. As time went by, durability was the prevalent argument. The Nineties, corresponded to the request of technicality and performance in the product. Since then, major medical crises have taken place (ESB) and from now on innocuisness in the product, is a major concern for the early 21st century consumer.

Innocuisness: "quality of what is not harmful" by this concept, one intends to make sure that the product does not contain chemical substances (synthetic or natural) which could have a harmful effect on health of the consumer.

The toxic, mutagen, carcinogen products were the first required products that led the European Union to publish several Directives prohibiting or limiting the use of these chemical substances (Directive 99/51/CE **[2]** concerning the pentachlorophenol, Directive 2002/61/CE **[3]** prohibiting the azo dyes...)

During the last years , the laboratories of analysis of leather were thus brought to develop new methods of chemical analyses to have tools making it possible to check the conformity of the rejections or the products compared to the new European directives.

Thus the chemistry laboratories of CTC **[4]** set up new analytical techniques: ICP/OES, ICP/MS, GC/MS, GC/ECD, HPLC/FLUORIMETRE HPLC/ DAD ETC... So methods were developed to analyze products as varied as, the azodyes, the bromodiphenylated ethers, the organotin compounds, the multi-residue methods.

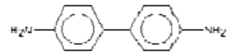
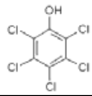
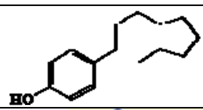
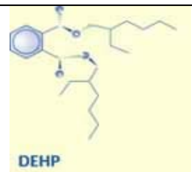
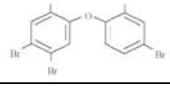
We propose to clarify the synergy between the development of chemical analyses methods dedicated either to the environment or with innocuisness.

II LEGISLATION

II.1 Innocuisness

Nowadays, many European legislations exist concerning leather and other materials used usually in the leather sector. These texts define the products (shoe, leather...) the chemical substances, but also the conditions of use (produced in contact with the skin, thin layer...).
Table 1 gives a non exhaustive list of the chemical substances most usually required.

Table 1: Innocuisness list of chemical Substances usually required

Chemical substances	Material / product	legislatif text	Example of molecule
Azo dyes	Leather and textile	Directive 2002/61/CE **[3]**	Benzidine 
Nickel	Metallic Element	Directive 94/27/CE **[5]**	
Polychlorophenols	Leather and textile	Directive 99/51/CE **[2]**	Pentachlorophenol 
Cadmium	Polymer (PVC)	Directive 91/338/CE **[6]**	
Chromium VI	individual protection of equipments	Directive 89/686/CE **[7]**	
Nonylphenol	Leather and textile	Directive 2003/53/CE **[8]**	
Phtalates	Plasticizers of PVC	Directive 2005/84/CE **[9]**	
Bromodiphenylated ether	Leather, textile, Synthetic	Directive 2003/11/CE **[10]**	Pentabromodiphenylated- ether 
Chloroalcans	shoes	Decision CEE 1999/179/CE (Ecolabel) **[11]**	
Organotins compounds	Leather, textile, plastic	Directive 76/769/CE **[12]**	

II.2 Parent directive water

Directive 2000/60/CE **[1]** of the European Parliament and the Council of October 23, 2000, established a framework for a Common policy in the field of water, wich it was transcribed in French law by the law of April 21, 2004. It aims at maintaining or restoring ecological and chemical quality, thus avoiding a deterioration of surface water and subsoil waters in Europe.

The recent adoption of this directive establishes a framework for a Common policy in the field of water and points out the orientations related to the good state of the watery ecosystems. It must be in consistency with the objectives of water protection. A list of "dangerous priority substances " was defined (see table 2). The ultimate objective of the directive is the improvement of the quality of natural environments by the suppression of these substances.

The identification as a dangerous priority substance reflects the intrinsic dangerous properties of a substance. It indicates that it is "toxic, persistent and bioaccumulable" or that it "is considered to an equivalent degree, like prone to guarantee".

The list drawn up by the European Directive refers to 33 substances (table 2.).
In France, the Ministry for Ecology and Durable Development brought the European list up to 87 substances. Indeed, at the time of the installation of the preceding European text, a list of 132 substances constituted the reference frame. The MEDD wished to continue monitoring certain substances in the list of the 132 and it to the list of the 33.

Table 2 : List of the dangerous substances

33 Substances		Complementary substances	
1.	Alachlor	101.	PCB 28
2.	Anthracene		PCB 52
3.	Atrazin		PCB 101
4.	Benzen		PCB 118
5.	Diphenylbrominated ether		PCB 138
6.	Cadmium		PCB 153
7.	C10-C13 Chloroalcanes		PCB 180
8.	Chlrofinvenfos	109.	1,2,4,5-Tetrachlorobenzene
9.	Chlorpyrifos	4ème liste	Hexachloropentadiene
10.	1,2-Dichloroethan	28.	1-Chloro-2-nitrobenzene
11.	Dichloromethan	29.	1-Chloro-3-nitrobenzene
12.	DEHP	30.	1-Chloro-4-nitrobenzene
13.	Diuron	24.	4-Chloro-3-methylphenol
14.	Endosulfan	33.	2-Chlorophenol
	(alpha-endosulfan)	34.	3-Chlorophenol
15.	Fluoranthen	35.	4-Chlorophenol
16.	Hexachlorobenzene	64.	2,4-Dichlorophenol
17.	Hexachlorobutadiene	122.	2,4,5-Trichorophenol
18.	Hexachlorocyclohexane		2,4,6-Trichorophenol
	(Lindane)	11.	Biphenyl
19.	Isoproutron	114.	Tributylphosphate
20.	Lead	78.	Epichlorhydrin
21.	Mercury	17.	2-Chloroaniline
22.	Naphtalen	18.	3-Chloroaniline
23.	Nickel	19.	4-Chloroaniline
24.	Nonylphenol	27.	4-Chloro-2-nitroanilin
	4-para-nonylphenol	52.	Dichloroanilin (3,4)
25.	Octylphenol	53.	1,2-Dichlorobenzene
	4-ter-octylphenol	54.	1,3-Dichlorobenzene
26.	Pentachlorobenzene	55.	1,4-Dichlorobenzene
27.	Pentachlorophenol	38.	2-Chlorotoluene
28.	HAP	39.	3-Chlorotoluene
	Benzo(a)pyrene	40.	4-Chlorotoluene
	Benzo(b)fluoranthene	20.	Chlorotoluene
	Benzo(k)fluoranthene	3ème list	Nitrobenzene
	Benzo(ghi)perylene	4ème list	2-Nitrotolouene
29.	Simazin	13.	Carbone tetrachloride
30.	Tributyltin compounds	36.	Chloroprene
31.	Trichlorobenzen		3-Chloroprene
	1,2,4-Trichlorobenzene		1,1-Dichloroethane
32.	Trifluralin		1,1-Dichloroethlyne
			1,2-Dichloroethlyne
			Hexachloroethane
			1,1,2,2-Tetrachloroethane
			Tetrachloroethylen
			1,1,1-Trichloroethane
			1,1,2-Trichloroethane
			Trichloroethylene
			Chlorure de vinyl

In order to set up a follow-up of the emissions of these substances in France, the ministry for Ecology and Durable Development (MEDD) decided to launch an analysis campaign to draw up an item zero and a list of classified installations to be controlled. The tanneries were part of these lists.

Let us notice that the majority of the substances in Table 1 are found in Table 2. Consequently, the objective was to carry out developments of methods to analyze these compounds in the waste water and CTC used its knowledge to make "leather" to develop analytical multi residus technics on the analysis of water. The study relates to some substances with very different physicochemical properties. We find there some organometallic compounds, metal elements, volatile pesticides, organic compounds, etc. This makes it possible to better evaluate complexity of the study.

III ANALYSIS DEVELOPPED

III.1 New techniques

III.1.1 New extraction techniques

In order to be able to proportion such a variety of made up (Table 2), it was necessary first of all to develop new methods of preparation and extraction.

Research and development led us to invest new apparatuses such as: ·

- distillation systems (PCP in leathers analyze), ·
- microwave (azo dyes analysis, European project : AALARM, micro organic compounds in sludges, fat content in leather)
- soxtec (phtalate in PVC, extraction of leather)
- head space (COHV, BTEX)
- thermodesorption.

III.1.2 New analytical technique

GC/MS

Gas chromatography coupled to a mass spectrometer (GC/MS) formed part of the analytical methods used during developments. It makes it possible to carry out the qualitative proportioning of the aromatic amines, the quantitative proportioning of the organotin compounds, Bromodiphenylated ether, Phtalate and Phenol.

Mass spectrometry is an extremely significant technique of detection which makes it possible to determine molecular structures.

HPLC

The High Performance Liquid Chromatography (HPLC) facilitates the analysis of very large molecules, of thermolabile or fluorescent compounds. In the study, This technique is used with a detection UV with bar of diode with an aim at quantifying the azo dyes or phenyl urea.
This detector makes it possible either to vary the wavelengths hanging the analysis or simultaneously, in order to record the absorbance with several wavelength, the bases method of confirmation. Thus in addition to the recorded signal (chromatogram), this detector (as the mass) makes it possible to provide information which is able to be used for the identification of the required compound.

In the same way to this type of analysis, CTC has been brought to develop more and more " expertise" because of the problems of provisioning. Consequently CTC developped some analytical methods making it possible for example, to find the cause of problems of odor or discolouration thanks to complex techniques such as the fluorimetry, infra red and the head space analyses.

III.2 Analysis development

We will develop in this chapter the reflexions which led to the multi residus analysis of dangerous substances in the Parent directive Water (Table 2).

Our challenge was to develop a powerful method in order to extract and analyze a maximum of compounds at the same time in order to limit the number of analysis and to reduce costs imposed to the industrialists.

The first step was to classify the various compounds according to their physicochemical properties and to carry out a global analytical solution. Except for semi metals, it led to the determination of two types of family :

- the semi volatile and no volatile compounds
- volatile compounds

Then, based on the methods already developped at the point on the level of leather, the groups of micropollutants were split within these two great families.

Thereafter, it was necessary to anticipate the compounds which could have a similar behaviour at the time of the preparation of the sample of the multiresidus type. This by taking into account obviously, chemical properties such as thermolability, volatility, stability in acid medium or basic, degradation with the light...

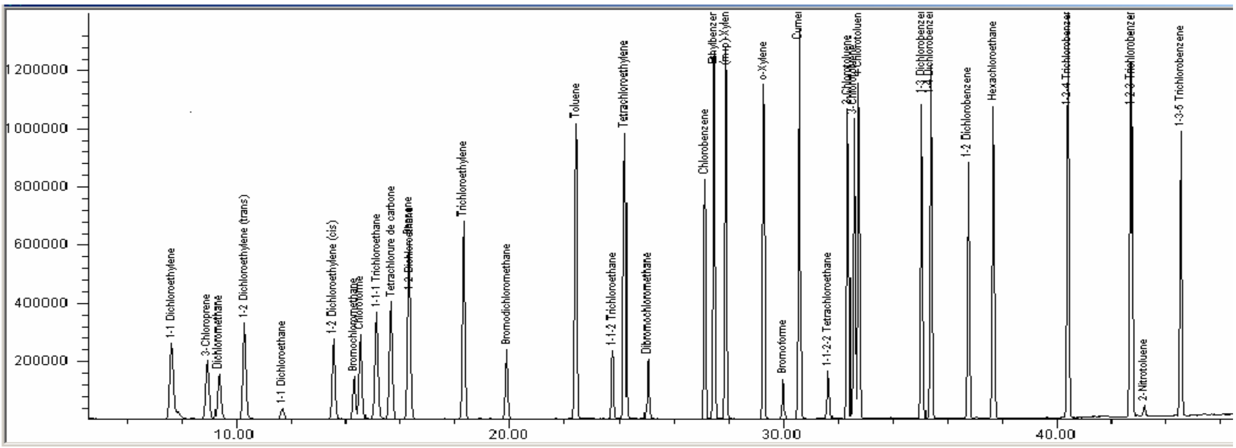
Once the substances were gathered by this mode of preparation, the objective was to determine the types of detection most adapted to quantify the compounds while keeping in mind a multi residus logic. To be in adequacy with this strategy of analysis (screening) and afterwards several tests, four groups were essential (Table 3):

Table 3 : Chemical families of compounds groups

	Familly of compounds	Analytical Standard
GROUP I	organochlorated Pesticids	EN ISO 6468 **[13]**
	organophosphorated Pesticids	EN 12918 **[14]**
	polychlorinated biphenyls	EN ISO 6468 **[13]**
	Phenol	EN 12673 **[15]**
	Triazines	EN ISO 10695 **[16]**
	Chloroanilines	
	Hydrocarbons Aromatics Polycyclic	EN ISO 17993 **[17]**
	Phenyl urea	EN 11369 **[18]**
	Phtalates	EN ISO18856 **[19]**
	Bromodiphénylated éther	ISO/CD 22032 **[20]**
	Misceallenous	
GROUP II	Tributyltin compounds	ISO 17353 **[21]**
GROUP III	$C_{10} – C_{13}$ Chloroalcanes	
GROUP IV	Aromatic volatile compounds	EN ISO 11423-1 **[22]**
	halogenated volatile compounds	EN ISO 10301 **[23]**

Once the global solution was carried out, it was necessary to enter in detail either the preparation of the sample or the optimization of the chromatographic parameters by keeping in mind the approach multi residue. For certain groups, there are normative references concerning the preparation of the sample: group IV and II. Nevertheless, for the volatile organic compounds, the optimization of the analysis was necessary in order to separate the compounds concerned with the Parent directive Water (Figure 1).

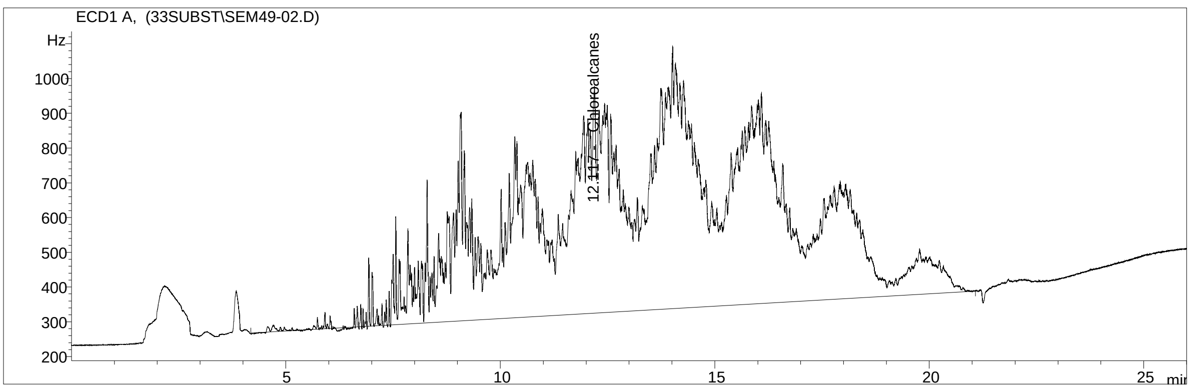
Figure 1 : Chromatogram of COV compounds (GC-HS-MS GROUP IV)



The analysis of organotins compounds as for it, had to be carried out several times to refine the quality of the analysis.

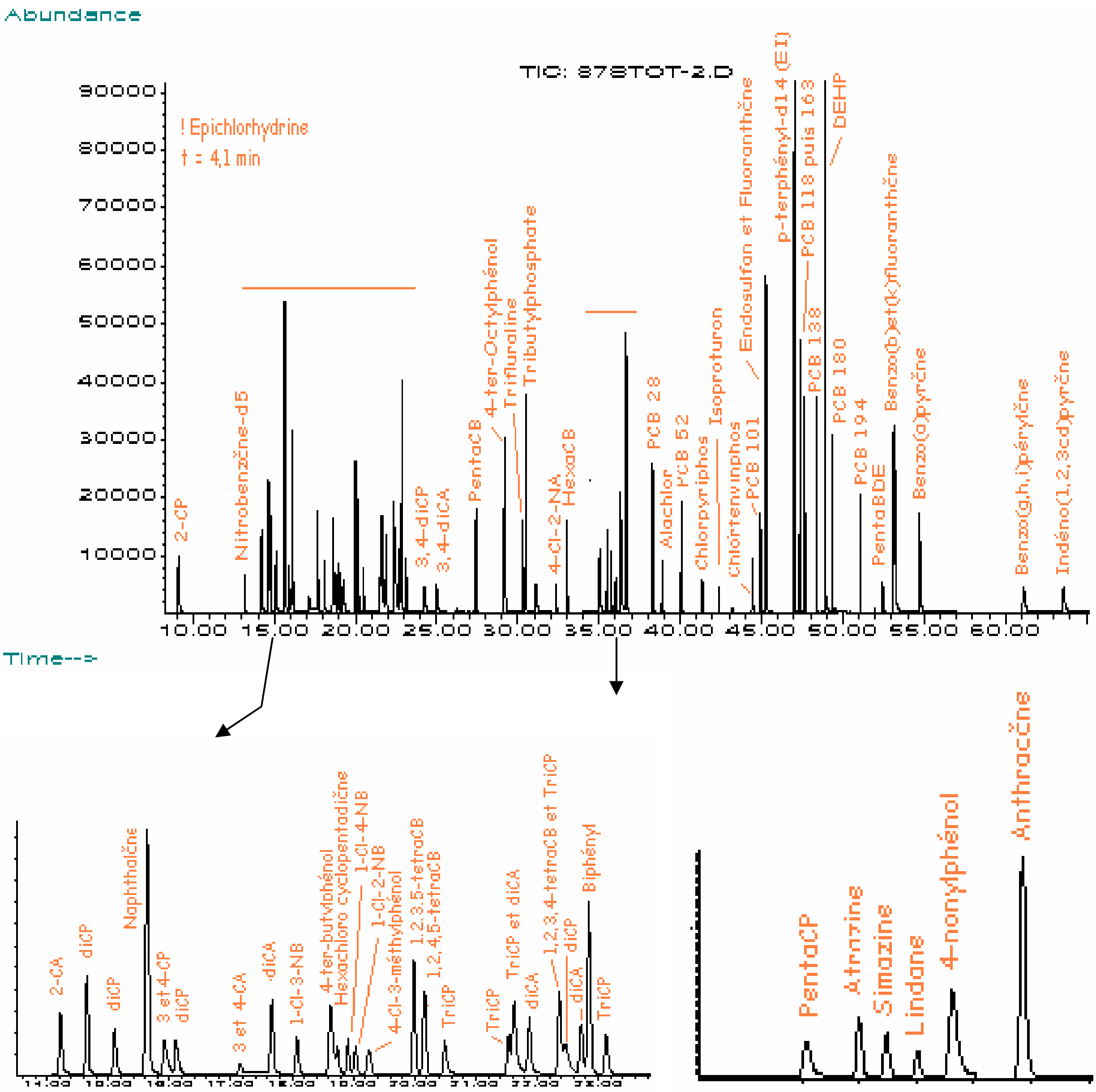
With regard to the analysis of the chloroalcanes C10, C13 (figure 2), the lack of reference involved the use of experimental designs in order to find a method of powerful preparation for the sample and initially the right, analytical technique to use,in the second time.

Figure 2 : Chromatogram of chloroalcan compounds (GC-ECD GROUP III)



Lastly, the last group of compounds was the one which required the most reflexion although normative references exist for certain substances. Indeed, the difficulty of the multi residue approach was to find on the one hand a preparation of the sample powerful enough, according to the chemical properties of the compouds (indeed the analysis gathers phenols, Triazines, organochlorinated and phosphorated pesticides) and on the other hand, a good quality of analysis (figure 3).

Figure 3 : Chromatogram of multi residu separation (GC-MS GROUP I)



For this last point it was necessary to introduce the concept of tracers and internal standards into the method of preparation, in order to be able to determine:

- a general output of the single extraction to the matrix considered
- a reproducibility of proportioning

Then, a reflexion further thougth needed to be given on the preparation of the samples.
Indeed, the objective was to find a solvent combination allowing the extraction of the compounds concerned by very diverse chemical properties. The use of experimental designs made it possible amongst other things, to vary this parameter, but also the pH and the quantity of solvent used according to the load of the matrix.
This led us to the choice of two different solvents used in acid media, basic and neutral and in quantities depending on the load of the matrix.

To conclude, Table 4 gives a summary of the analytical strategy installation.

Table 4 : Analytical Strategy

Group of substances	preparation	Analytical technic	Example of performance of the method in waste water : LQ
I	Liquide-liquide Extraction	GC-MS HPLC-DAD HPLC-fluorimeter	Naphtalene 0.05µg/l Atrazin 0.05µg/l DEHP 1µg/l
II	Derivatization and Liquide-liquide Extraction	GC-MS	TBT 0.01µg/l
III	Liquide-liquide Extraction	GC-ECD	Chloroalcane 5µg/l
IV	Head Space	GC-HS-MS	Tetrachloroethylene 0.5µg/l Benzene 1µg/l

Following the study undertaken as regards environmental analysis, CTC has from now on, a panel of methods making it possible to proportion a great number of substances potentially present in the effluents.

V. WASTE WATER IN TANNERIES RESULTS

Following the adoption of Directive 2000/60/CE, the Ministry for Ecology and Durable Development (MEDD) set up a study in France concerning 5000 factory sites. The object of this work is to constitute an item zero which will make it possible in the future to better evaluate the evolution of the aquatic environments and their attack of the standards of optimal environmental quality.

Obviously the activities of tanneries and megisseries were included in the list of the industrial facilities to be controled. Thus CTC was brought to analyze waste water of about thirty tanneries.

V.1 Protocol of realisation of a 87 substances control

The MEDD selects a company whose industrial activity is potentially polluting and which generates waste water.

The company chooses a chemistry laboratory which is accredited and counsel for the standard realization of the "87substances"analyses.

The laboratory carries out a preliminary visit to :

- estimate the quantities of MES (suspended matter).
- define the intake points “24hours”
- define the nature of waste
- define the drainage systems
- specify the dates and methods of intervention
- determine the substances suitable to be found during the study (because used in the company)

A preliminary report of the visit is written by the laboratory and is then addressed to the manufacture and to the MEDD. As soon as the report is agreed on the major part is done, the step measurement can start.

Figure 4: example of taking

The taking is carried out (see figure 4), the sample is collected and preserved at 4°C and conveyed in the 12 hours to the laboratory.
When the sample arrives to the laboratory, MES are analysed:

- if MES are lower to them than 500mg/l, the sample is analyzed such as
- if MES are higher than 500mg/l, the sample is centrifuged. The aqueous phase and the particulate phase are analyzed separately, the result of the analysis will be the sum of the quantities found in the 2 phases.

Once the test report is done, it is addressed to the industrialist and to the MEDD which will have 1 month to dispute it or ask for details or additional analysis.

V.2 Results

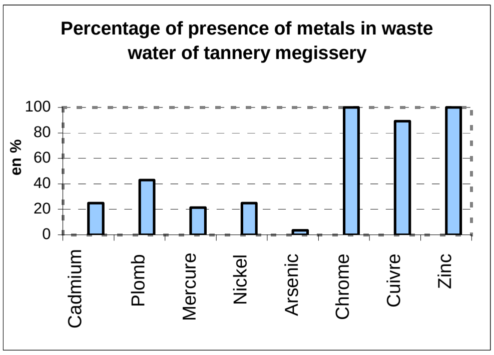
The results presented below will relate to 30 tanneries.
For each type of pollutants (metals, organic volatile compounds, organic not-volatile compounds), we determined :

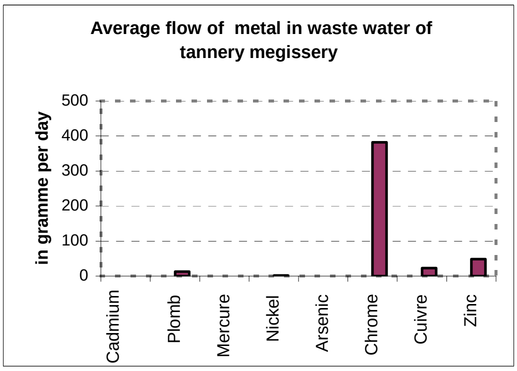
- the number of times that one could determine the presence of the substance considered in the effluents.We then expressed this number in % compared to the thirty tannery-megissery tested.
- For each detected substance, we determined a concentration. The matter flow is calculated by taking into account the flow. In fact the average flow of the 30 tanneries is reported below.

V.2.1 Metal analysis

The results observed for the analysis of metals (figure 5) indicate that the three elements most found in the rejections are, Chromium Copper and Zinc and that Chromium is the element which is found in great quantity. What does not constitute a surprise!

Figure 5: Results concerning metallic element

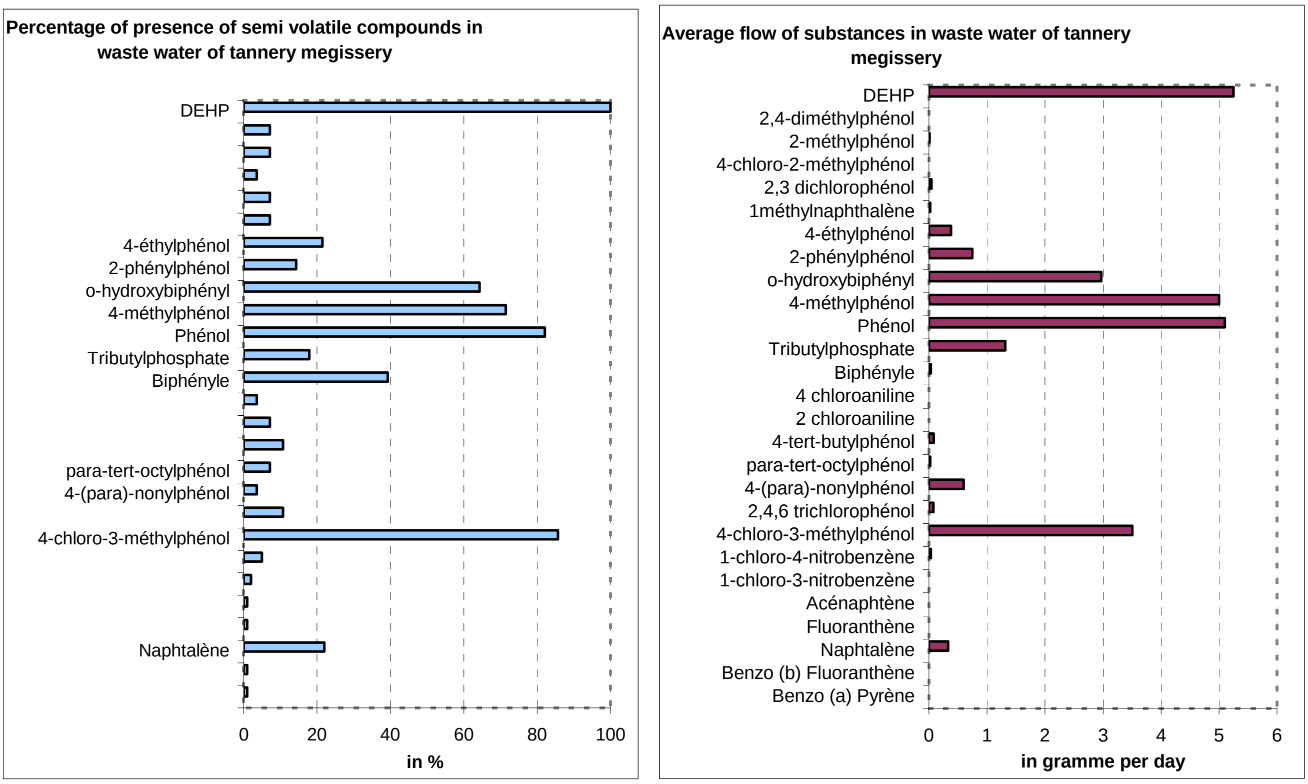




V.2.1 Organic micro-pollutants Analysis

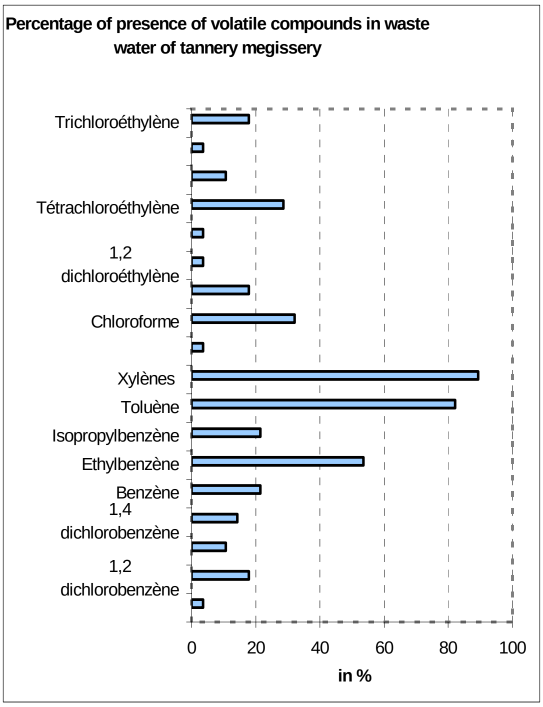
On the level of the multi residues analysis concerning the various families of substances (figure 6), it appears that certain phenols, naphthalene (aromatic hydrocarbon polycyclic) and diéthylhexylphtalate (DEHP) are the compounds most found. These substances come primarily from the used of dyes (phenols and naphthalen) and also from the PVC channel (DEHP).
Similarly, they are present in great quantity in the waste water of the 30 tanneries.

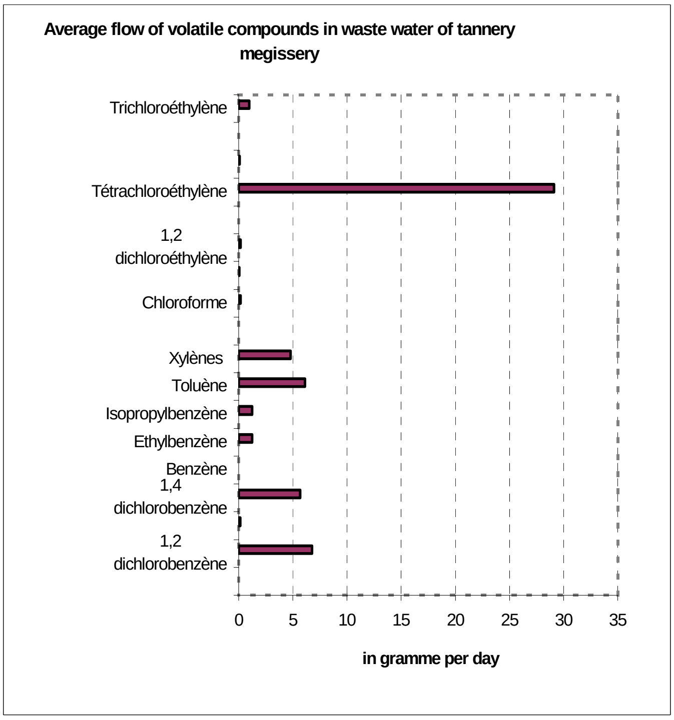
Figure 6 : Results concerning semi-volatile compounds:



Lastly, the analysis of the volatile compounds (figure 7) indicates the presence of aromatic compounds (benzene derivatives) and of tetrachloroethylene in the rejections, this last pretence largely majority compared to the other products.

Figure 7 : Results concerning volatile compounds





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