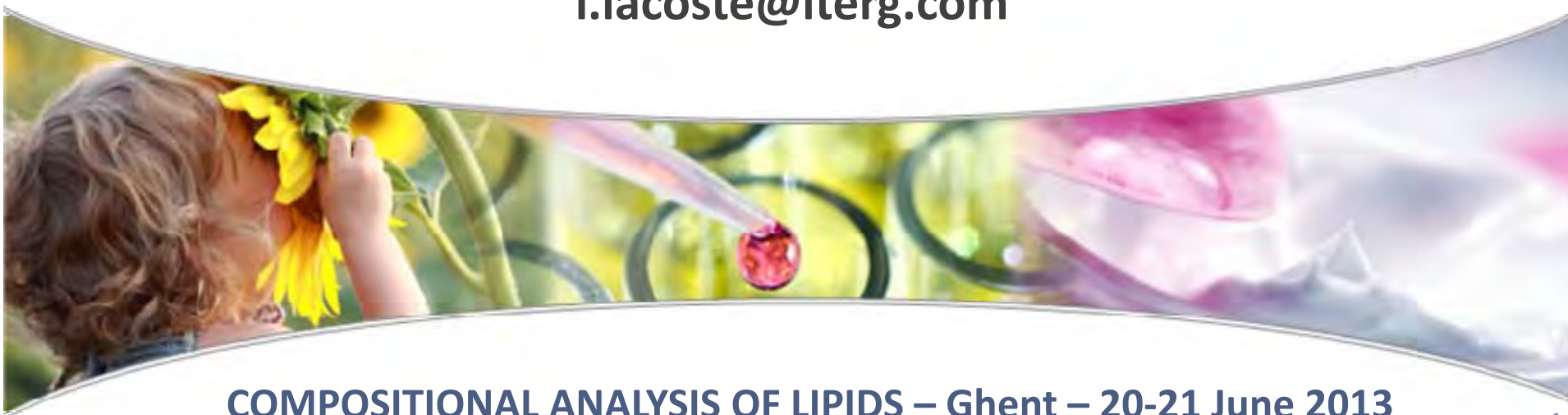
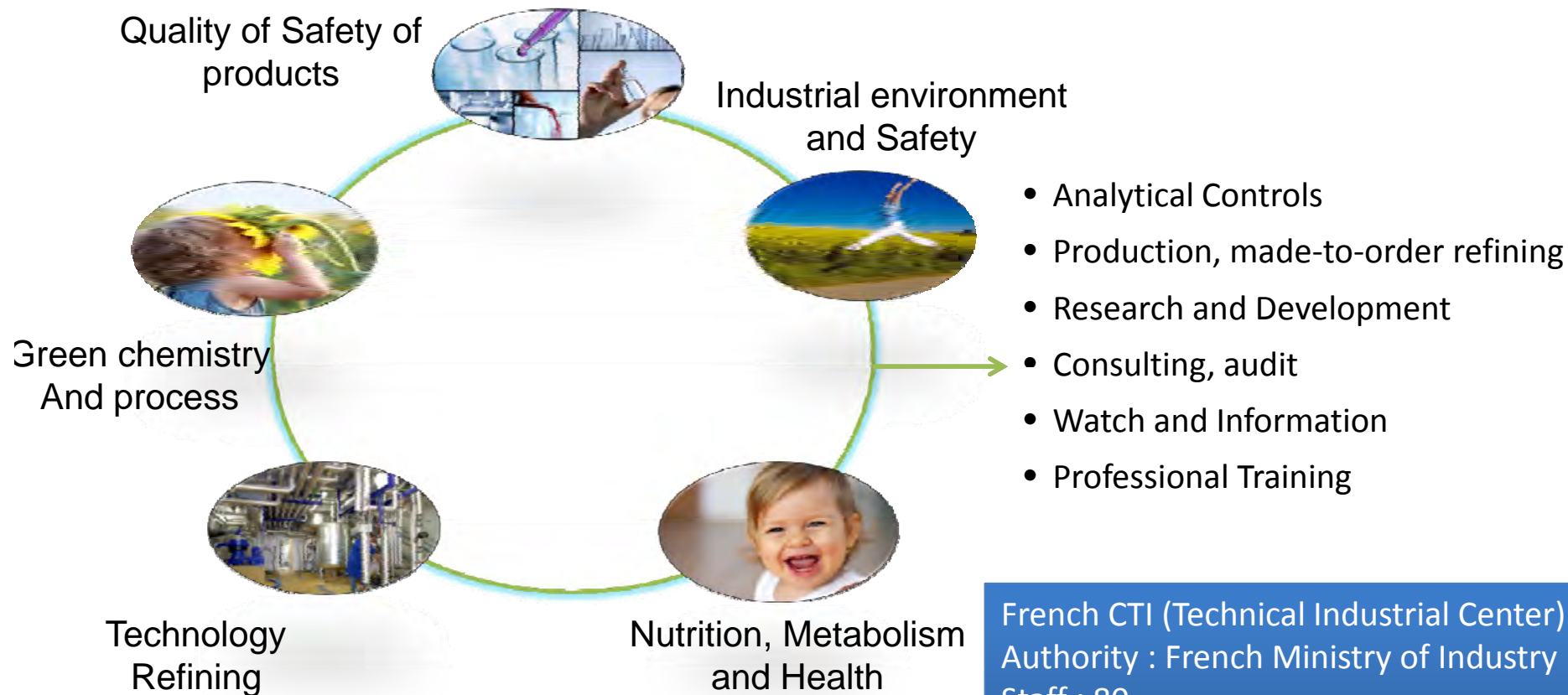


# Contaminants in oils and fats: analysis and regulations

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## A synergy of competences services provided



French CTI (Technical Industrial Center)  
Authority : French Ministry of Industry  
Staff : 80  
2012 Budget : 6M€  
ISO 9001 V 2008 & ISO 17025

# Contents

Heavy metals

Polycyclic aromatic hydrocarbons

Mineral oil

Phthalates

Regulation ?

Recognized analytical methods ?

Risks ?



# Origins of undesirable compounds

Environmental contamination  
metals, dioxins & PCBs, PAHs,  
**mineral oil**

Crop protection  
pesticide residues, **mineral oil**



Transport & storage  
phthalates, **mineral oil**

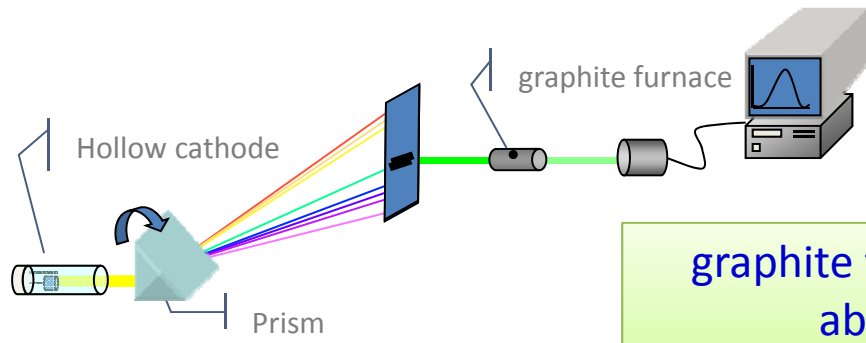
Production process  
PAHs, **mineral oil**, phthalates,  
3-MCPD esters & glycidol esters

# Heavy metals

- Environmental contamination (air, soil)
- Regulation & International Food Standard
  - Codex Standard 193-1995
  - (EC) n°1881/2006 – contaminants in foodstuffs



# Metals : methods & regulations



graphite furnace atomic absorption

inductively coupled plasma optical emission

## Analytical methods

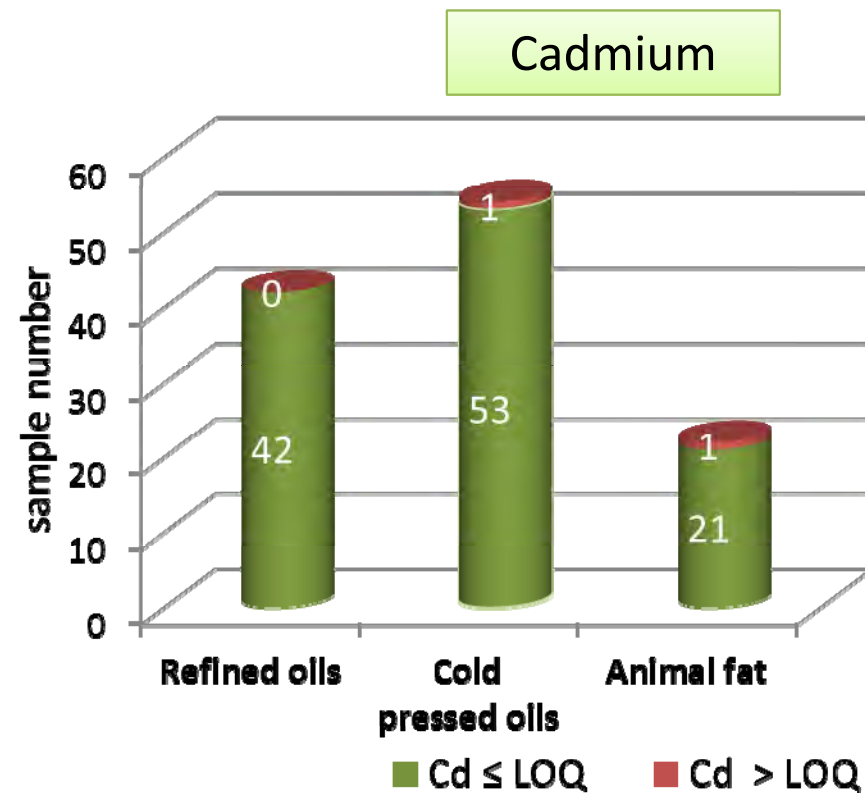
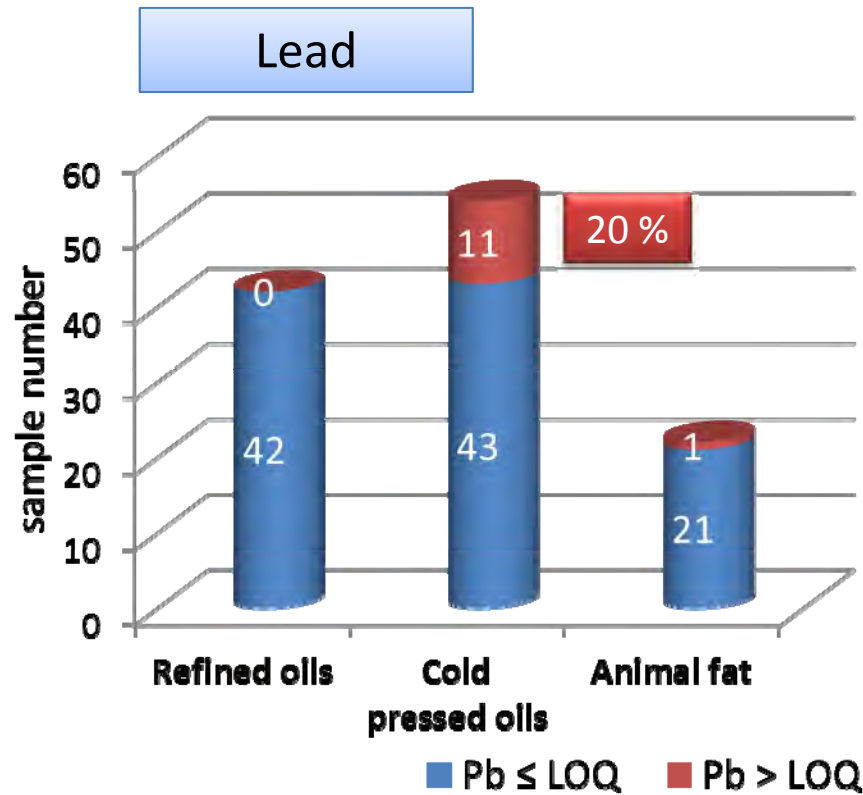
ISO 8294 → Cu, Fe, Ni  
ISO 15774 → Cd  
ISO 12193 → Pb

ISO/TS 21033 → Cd, Pb, Cu, Fe, Ni

METALS	Cd	Pb	Ni	As	Cr
LOQ atomic absorption (mg/kg)	0,002	0,010	0,015	0,010	0,005
Regulation limit for oils (mg/kg)	-	0,10 EU&Codex	0,2 France	0,1 Codex	0,05 France

# Metals : occurrence in edible oils & fats

Lead may be present in some cold-pressed oils

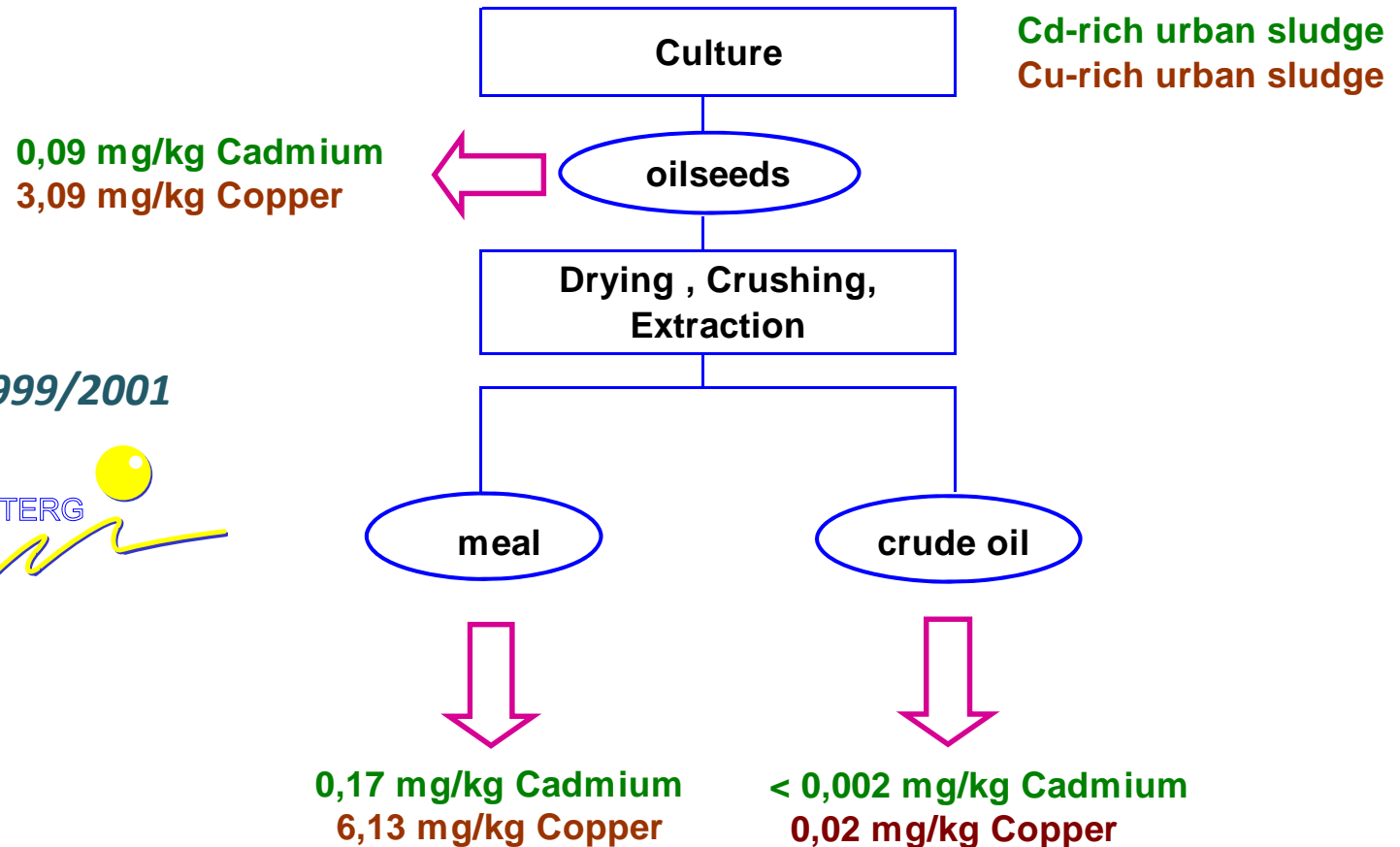


ITERG data (1992 -1999)

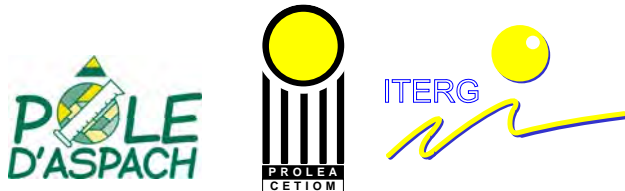


# Heavy metals transfer from soil to rapeseed oil

Metals in the seeds are transferred to meals after seed crushing



ADEME Project – 1999/2001

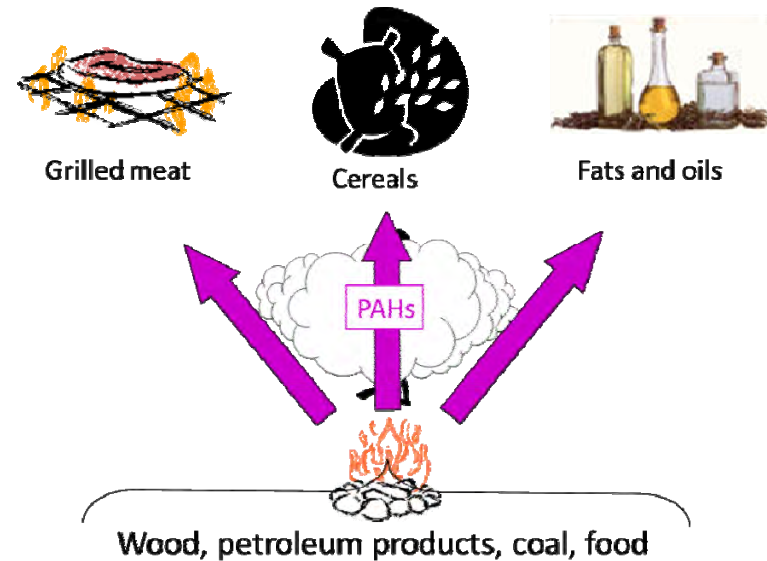




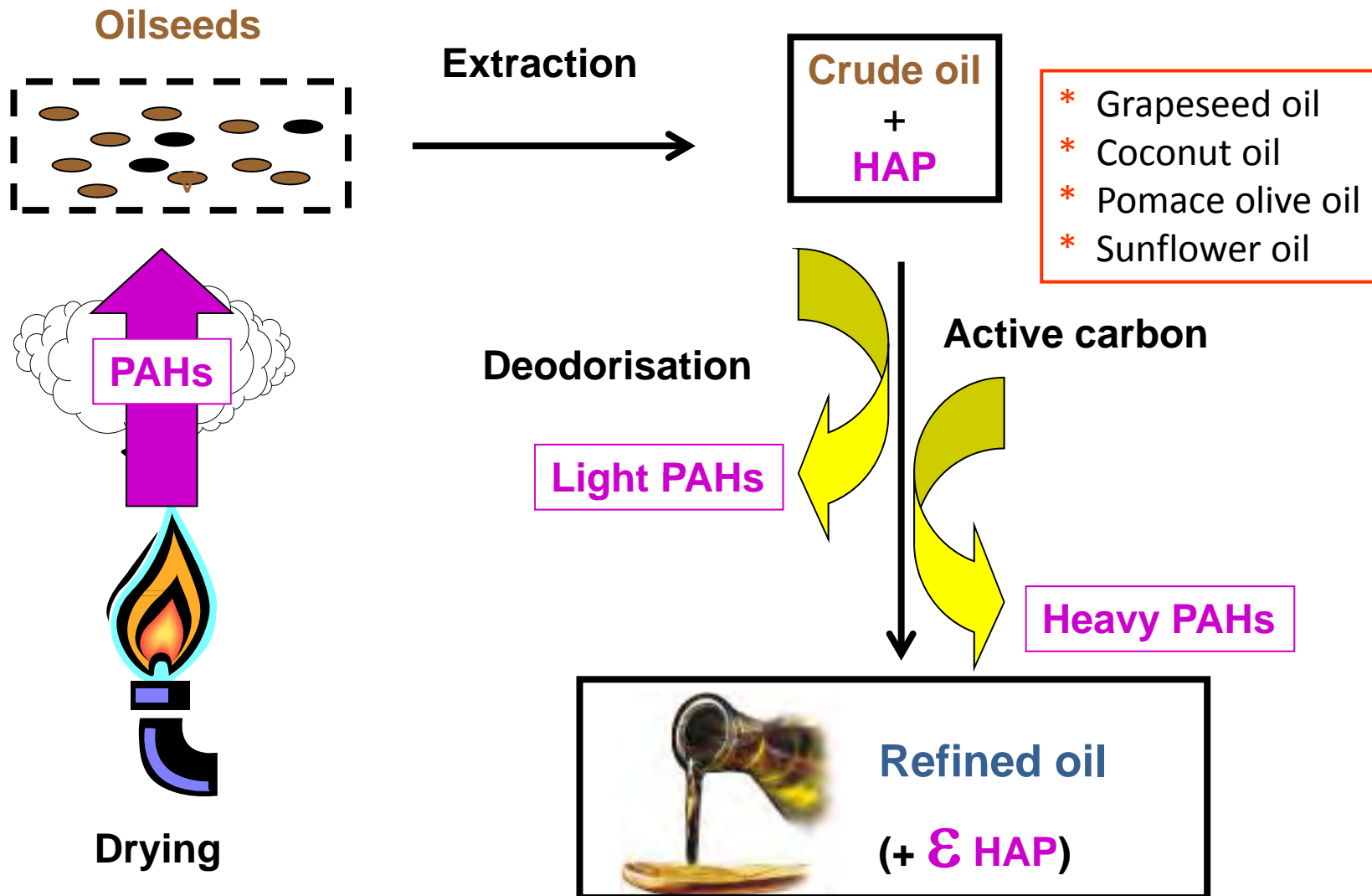
# Polycyclic aromatic hydrocarbons

- Environmental contamination
- Production process
- Regulation

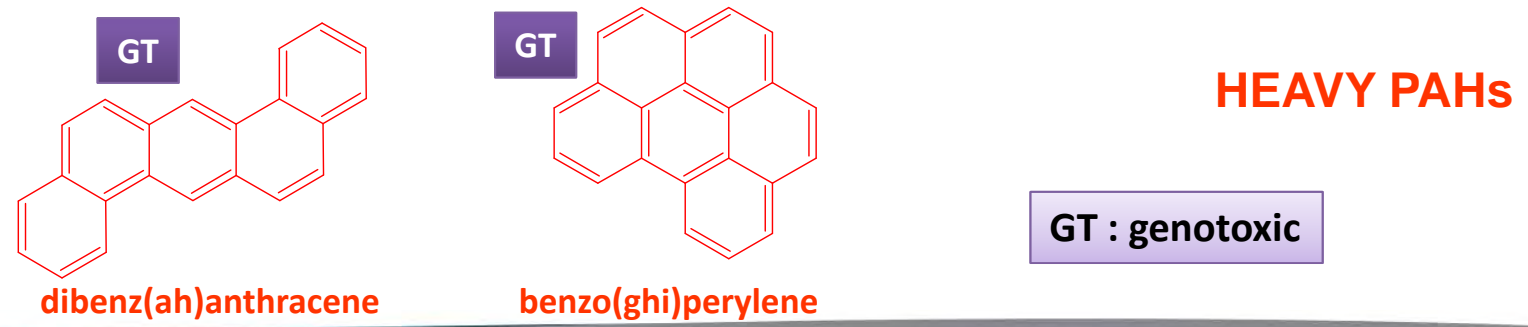
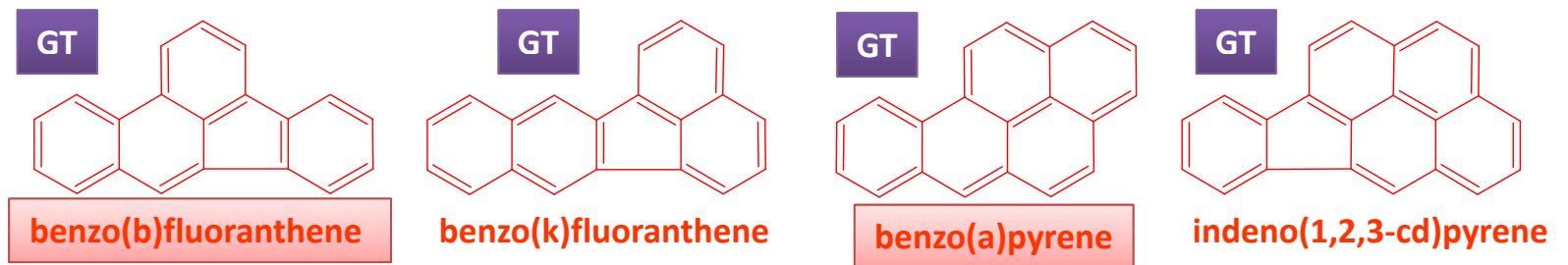
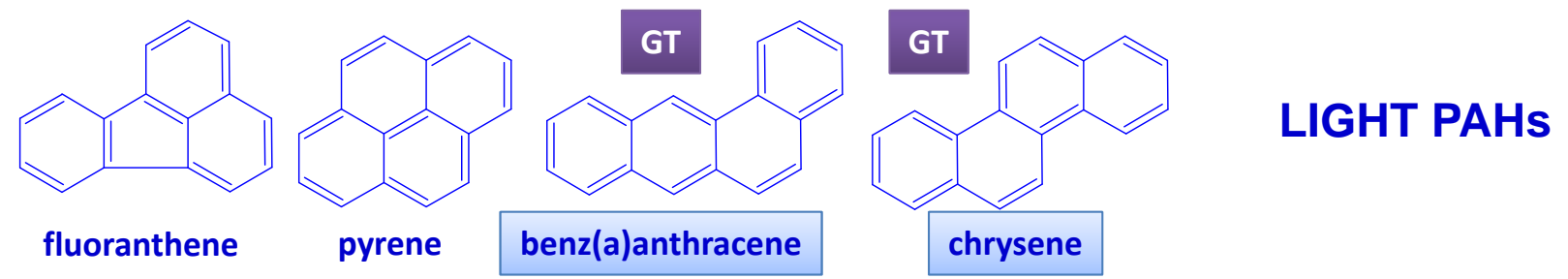
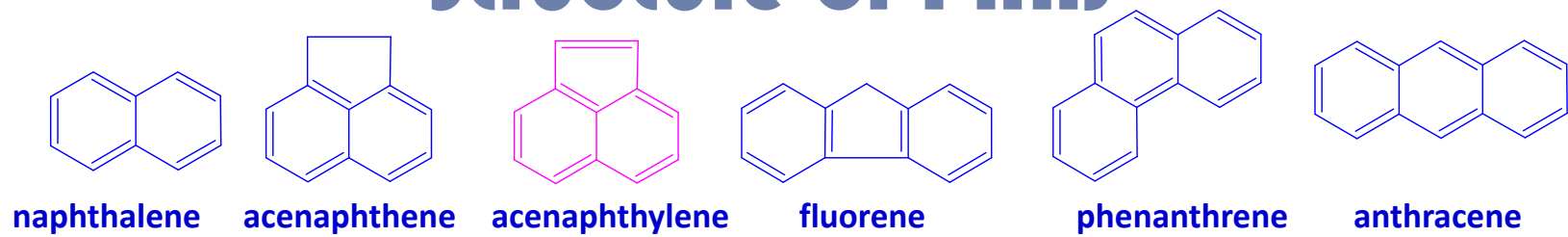
→ (EC) n°1881/2006 – contaminants in foodstuffs



# PAHs origins in vegetable oils



# Structure of PAHs



**GT : genotoxic**

# PAHs regulation: (EC) n° 1881/2006 contaminants in foodstuffs

PAHs	Maximum levels oils and fats (µg/kg)	Maximum levels coconut oil (µg/kg)	Maximum levels cocoa butter (µg/kg)
<b>Sum of 4 PAHs:</b>			<b>35,0</b>
- benzo[a]pyrene			<i>from 1.4.2013</i>
- benz[a]anthracene	<b>10,0</b>	<b>20,0</b>	<i>until 31.3.2015</i>
- benzo[b]fluoranthene			<b>30,0</b>
- chrysene			<i>from 1.4.2015</i>
<b>benzo[a]pyrene</b>	<b>2,0</b>	<b>2,0</b>	<b>5,0</b> <i>from 1.4.2013</i>

# PAHs: determination methods

## Principle

- ✓ **PAH isolation:** liquid chromatography (alumina, silica gel, C18-silica gel) or HPLC (donor-acceptor complex chromatography, size-exclusion chromatography)
- ✓ **Analysis:** HPLC/fluorescence or GC/MS

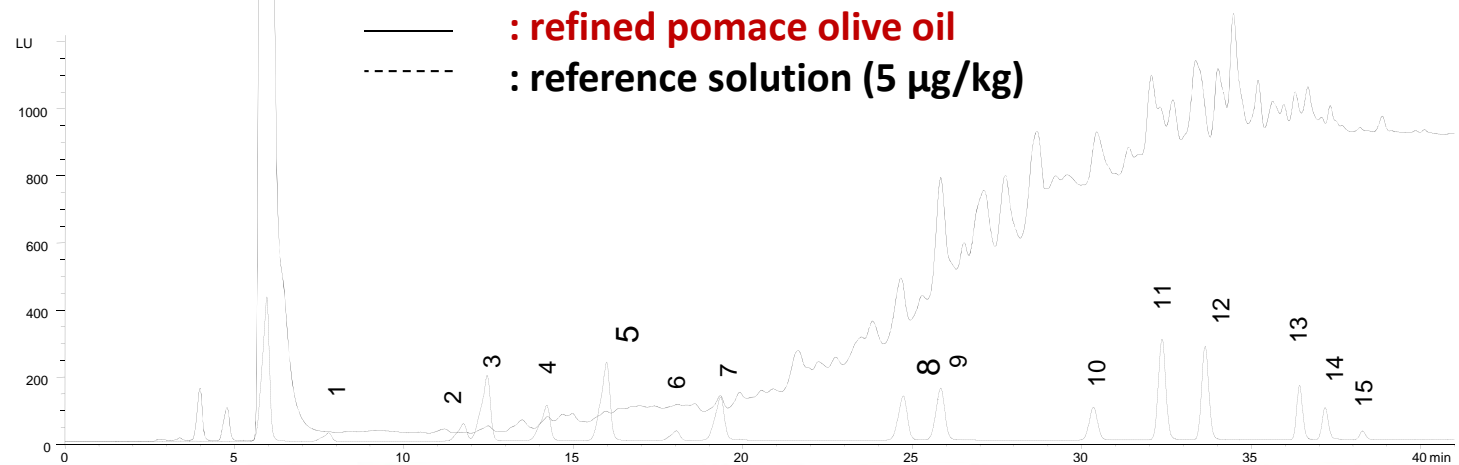
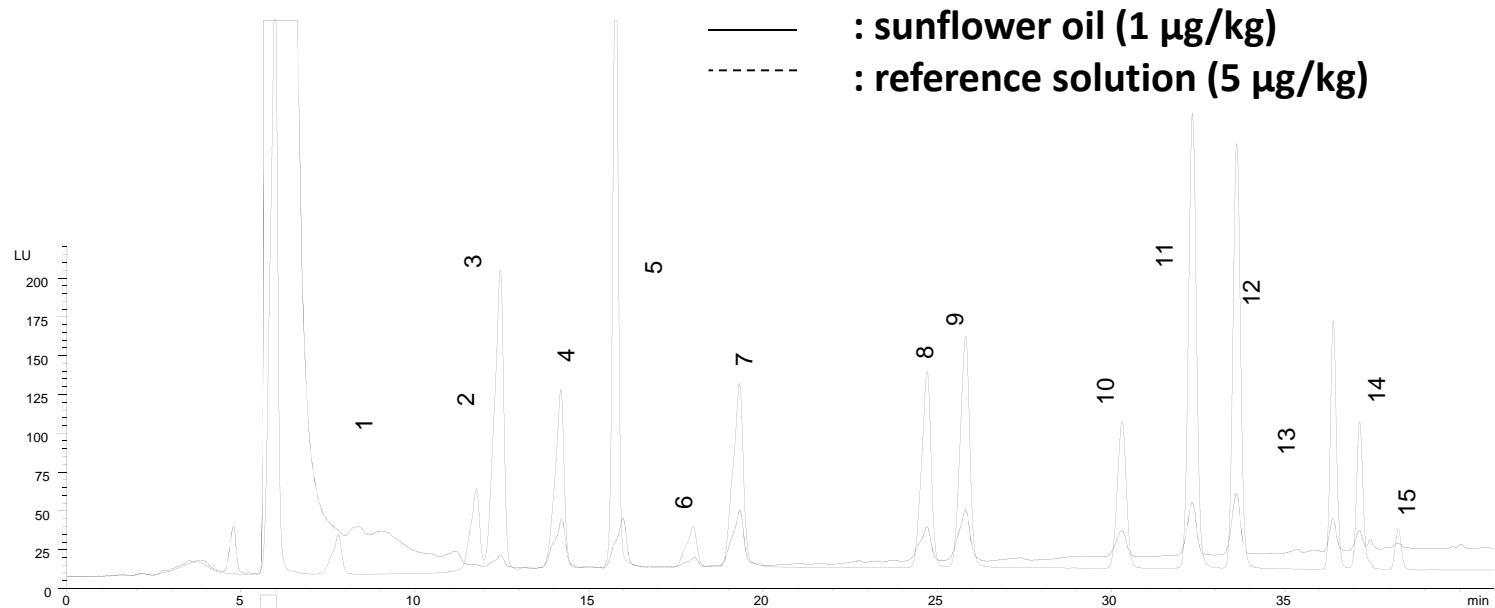
ISO 15302 : benzo[a]pyrene in oils (LC + HPLC/FLD)  
ISO 15753 : 12 PAHs in oils (2 SPE + HPLC/FLD)  
ISO 22959 : 17 PAHs in oils (DACC on-line + HPLC/FLD)  
EN xxxx (JRC) : 4 PAHs in foodstuffs (SEC + SPE + GC/MS)

Method	ISO 15302	ISO 15753	ISO 22959
BaP LOQ ( $\mu\text{g}/\text{kg}$ )	0,1	0,2	0,1
Reproducibility (CVR%)	27 % (2,1 $\mu\text{g}/\text{kg}$ )	41% (3,21 $\mu\text{g}/\text{kg}$ )	10 % (2,6 $\mu\text{g}/\text{kg}$ )

# PAHs: some difficult matrixes

ISO 15753

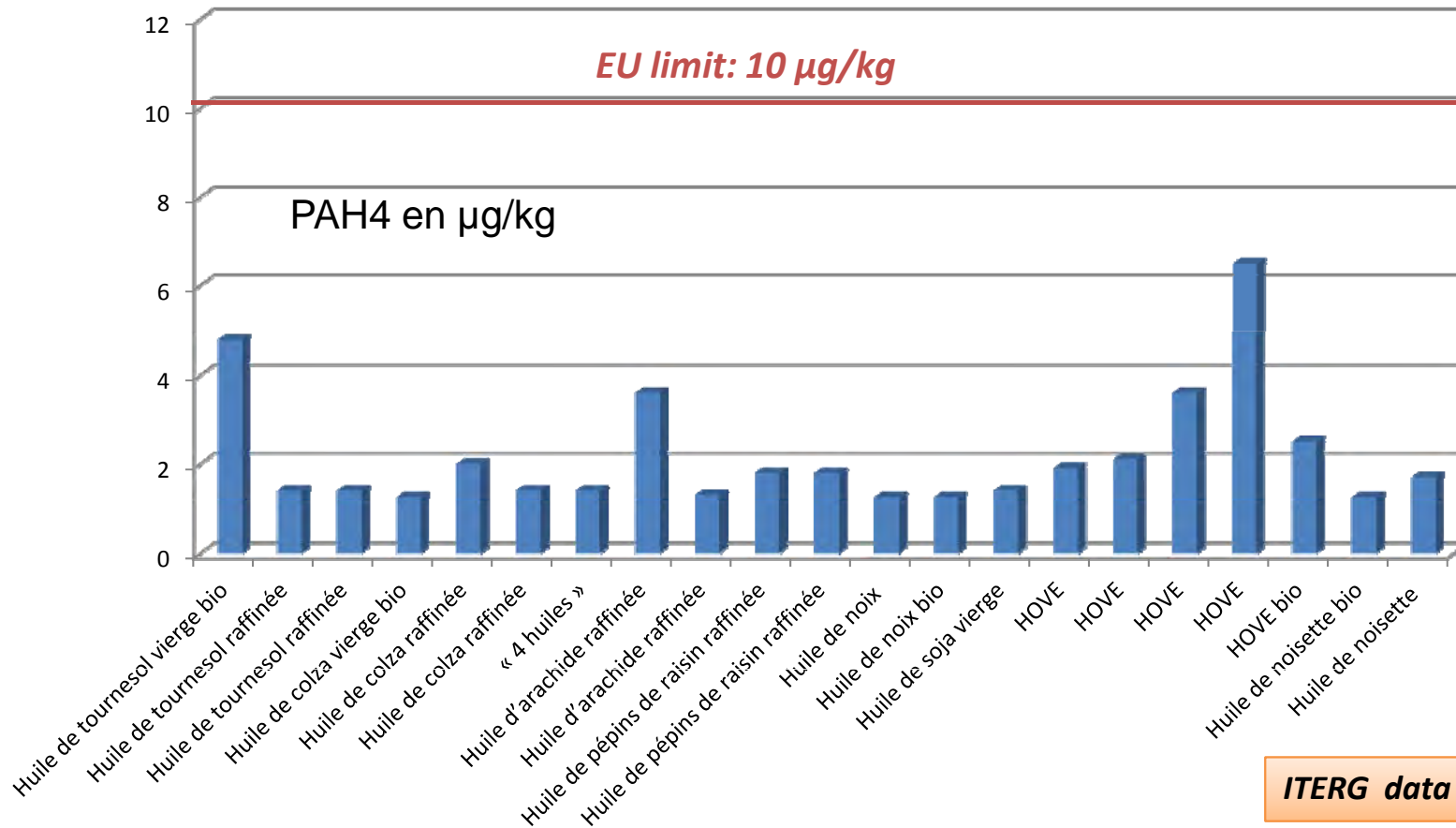
- (1) NA
- (2) AC
- (3) FL
- (4) PHE
- (5) ATR
- (6) FA
- (7) PY
- (8) BaA
- (9) CHR
- (10) BbFA
- (11) BkFA
- (12) BaP
- (13) DBahA
- (14) BghiP
- (15) IP



# Edible oils: PAH4 levels

## Screening 2012 : 21 vegetable oils

benzo(a)pyrène  
 chrysène  
 benz(a)anthracène  
 benzo(b)fluoranthène



**ITERG data (2012)**



# Mineral oil

- Environmental contamination (air, soil)
- Crop protection
- Transport & storage
- Production process
- Regulation

→ (EC) n°1151/2009 - import of sunflower oil from Ukraine

→ EFSA Scientific Opinion on Mineral Oil Hydrocarbons in food (2012)



# Mineral oil composition

## EFSA Scientific Opinion, 2012

Mineral oil: complex mixture of hydrocarbons

→ MOSH: straight or branched alkanes & alkylated cycloalkanes

→ MOAH: aromatic hydrocarbons including alkyl-substituted

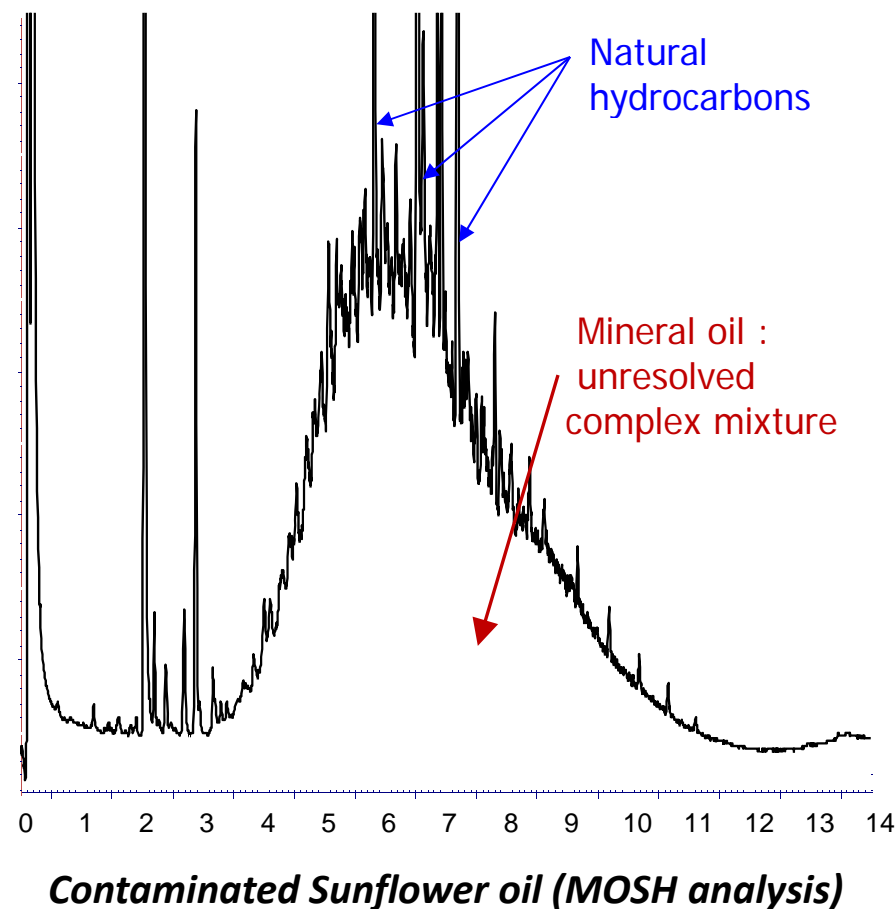
Hydrocarbon compound number in mineral oil > 100 000 for those with less than 20 carbon atoms !

Different products & composition: diesel fuel, white oil, lubricant ...

Technical grade mineral oil contain 15-35 % MOAH, which is minimised in food grade MOSH (white oils)

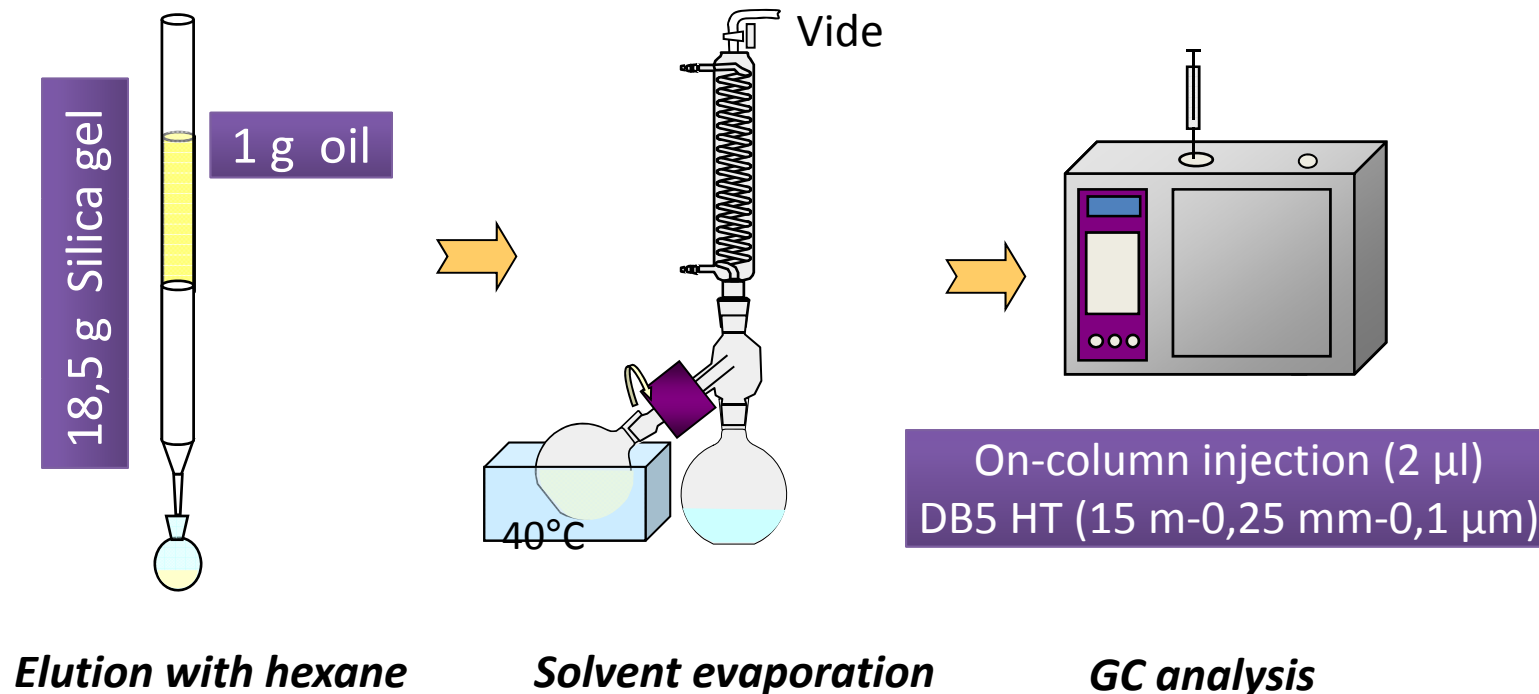
# Mineral oil detected in vegetable oils

- 2008 → contamination of sunflower oil from Ukraine with a mineral oil from unknown origin
- 2009 → contamination of walnut oil with a food grade lubricant oil during refining process
- 2010 → identification of compounds eluted as mineral oil in grapeseed oils
- 2011 → contamination of milk fat with a food grade lubricant oil during production



# MOSH determination: ISO/ CD 17880

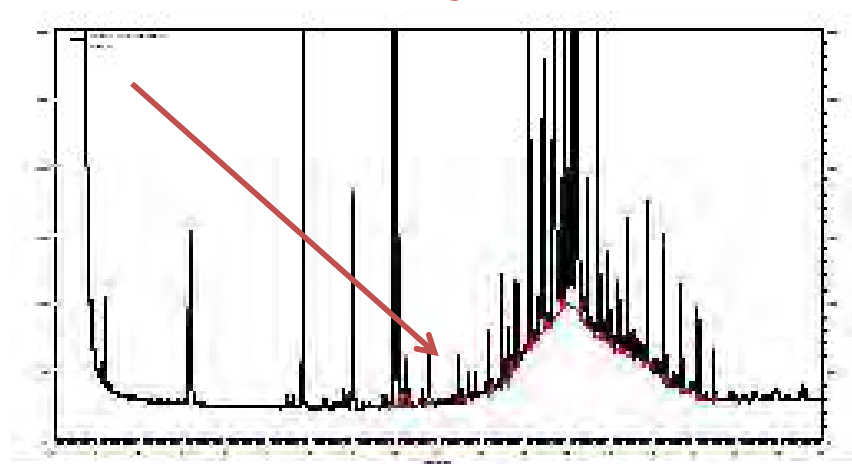
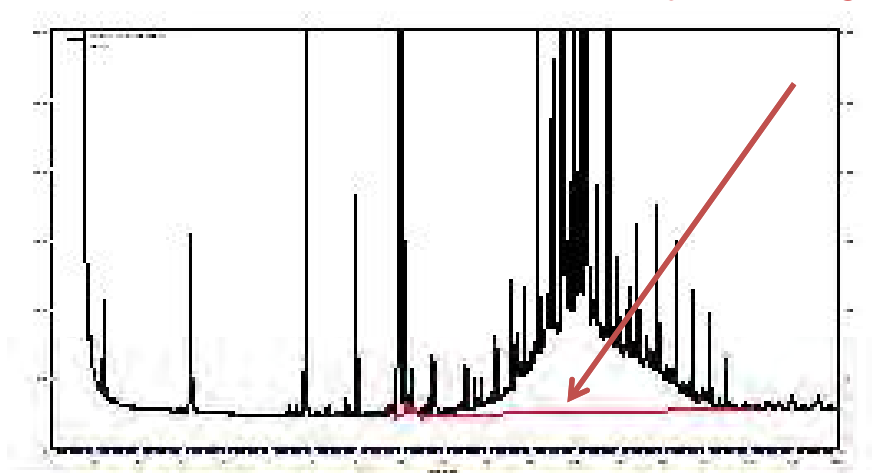
- Fractionation of the sample by liquid chromatography on silica gel or silica gel impregnated with  $\text{AgNO}_3$
- Quantification with an internal standard (C18 or C20)
- GC/FID analysis on an short apolar column



# MOSH determination: critical points

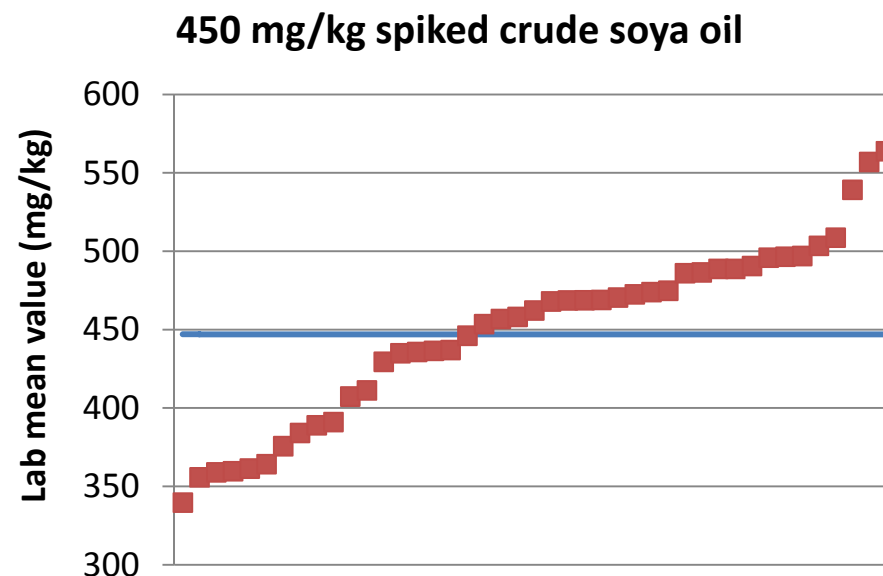
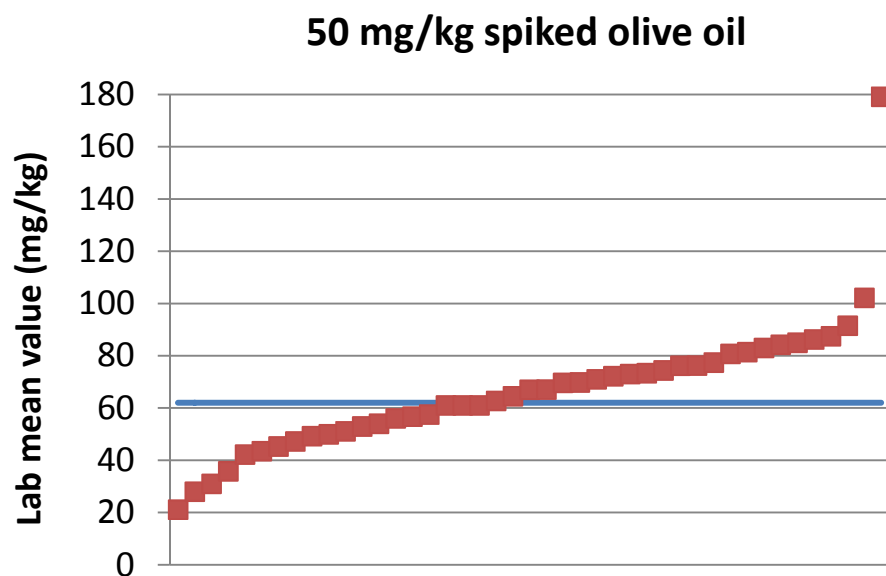
- Cross contamination to be avoided
- Quantification of C10 to C50 without losing the volatile hydrocarbons
- Analysis of all types of samples (crude, refined, vegetable & animal oils & fats)
- Limit of quantification as low as possible
- Integration of the hump & subtraction of the “natural hydrocarbons”

*It is necessary to integrate twice the chromatogram*



# Mineral oil determination: ISO/ CD 17880 pre-collaborative trial

43 participants from 12 countries (2012) → dispersed results



Laboratories

Laboratories

sample	olive oil	crude soya oil
mean value (mg/kg)	62	447
reproducibility (mg/kg)	49	153
Horrat value	3,3	1,9

# Phthalates

- Transport & storage

- Production process

- Regulation

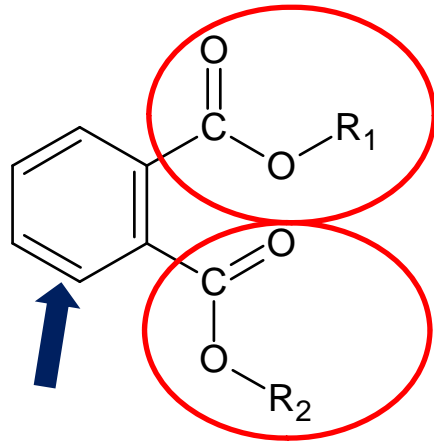
- EFSA Scientific Opinion on food additives, flavourings, processing aids and materials in contact with food (2005)

- (EC) n°10/2011 - plastic materials and articles intended to come into contact with food





# Chemical structures of phthalates



## DEHP

- Oily visquous liquid
- MW: 390,6 g/mol
- BP: 385°C
- Water solubility: 3 µg/l
- High affinity for fat (log Kow : 7,5)

Di-methyl PHT	DMP	R1=R2=methyl
Di-ethyl PHT	DEP	R1=R2=ethyl
Di-isobutyl PHT	DIBP	R1=R2=isobutyl
Di-butyl PHT	DBP	R1=R2=butyl
Di-hexyl PHT	DHexP	R1=R2=hexyl
Benzyl butyl PHT	BBP	R1=benzyl R1=butyl
Di-n-heptyl PHT	DHepP	R1=R2=heptyl
<b>Di-(2-ethyl hexyl) PHT</b>	<b>DEHP</b>	<b>R1=R2=ethyl-2 hexyl</b>
Di-n-octyl PHT	DNOP	R1=R2=octyl
Di-isononyl PHT	DINP	R1=R2= isononyl
Di-isodecyl PHT	DIDP	R1=R2=isodecyl

# Phthalates are everywhere



Toys  
Child-care articles



Shoes-Boots-Gloves  
Out-door & rainwear



Car undercoating  
Dashboard-Door  
panels-Safety glass



Flooring-Roofing- Wall covering  
Adhesives-Sealant-Rubber  
Paints-Shower curtains  
Wires & cables-Fresheners



Cosmetics : Perfume  
Hairspray-Deodorant  
Skin emollient-nail polish  
fingernail elongators



Pharmaceuticals  
Medical devices :  
Catheters-Blood bag

# (EC) n° 10/2011 - Plastic materials & articles into contact with food

Specific migration limit in food		To be used as
BBP	30 mg/kg	Plasticizer in single-use material containing non-fatty foods except infant formulae
DINP	$\Sigma = 9 \text{ mg/kg}$	
DIDP		
DEHP	1,5 mg/kg	Plasticizer in repeated use materials containing non-fatty foods
DBP	0,3 mg/kg	



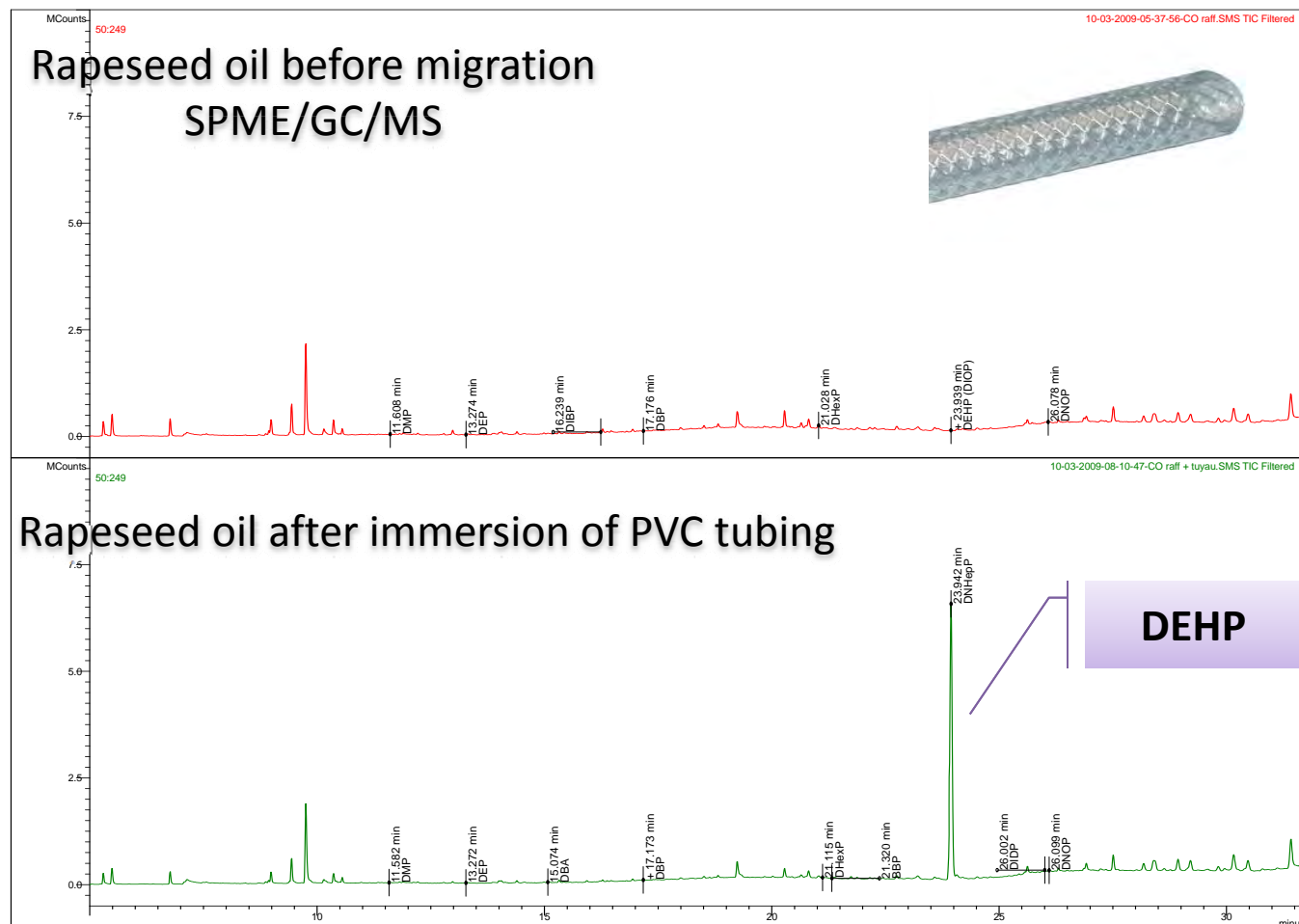
→ Material containing these phthalates cannot be used for oils & fats

Phthalates are not used in the manufacture of or the formulation of this product.

# DEHP migration in rapeseed oil (PVC tubing)

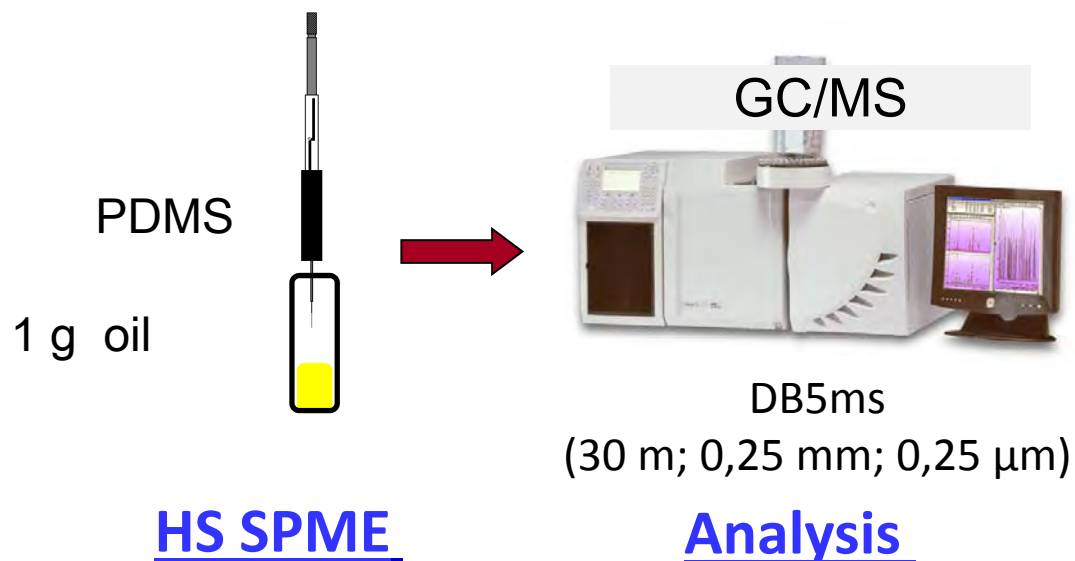
Chromatogram Plots

ITERG data, 2008

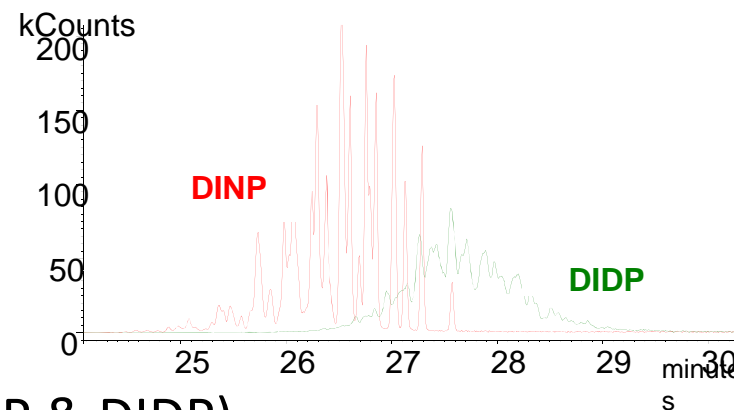
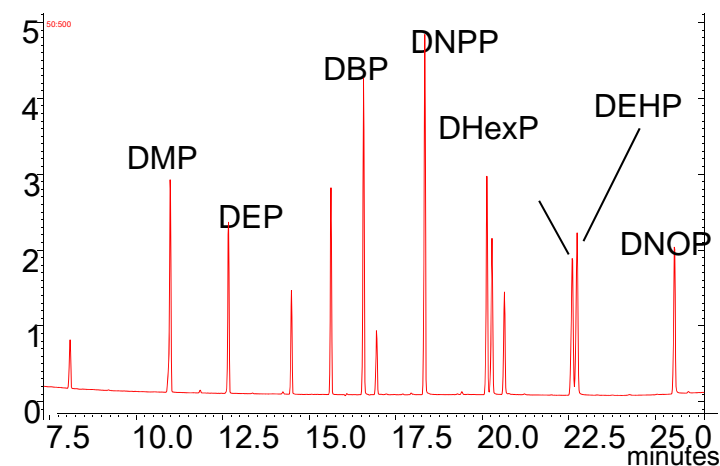


Oil sample kept in a bottling machine tub → 3 825 mg/kg of DEHP !

# Phthalates: ITERG's procedure



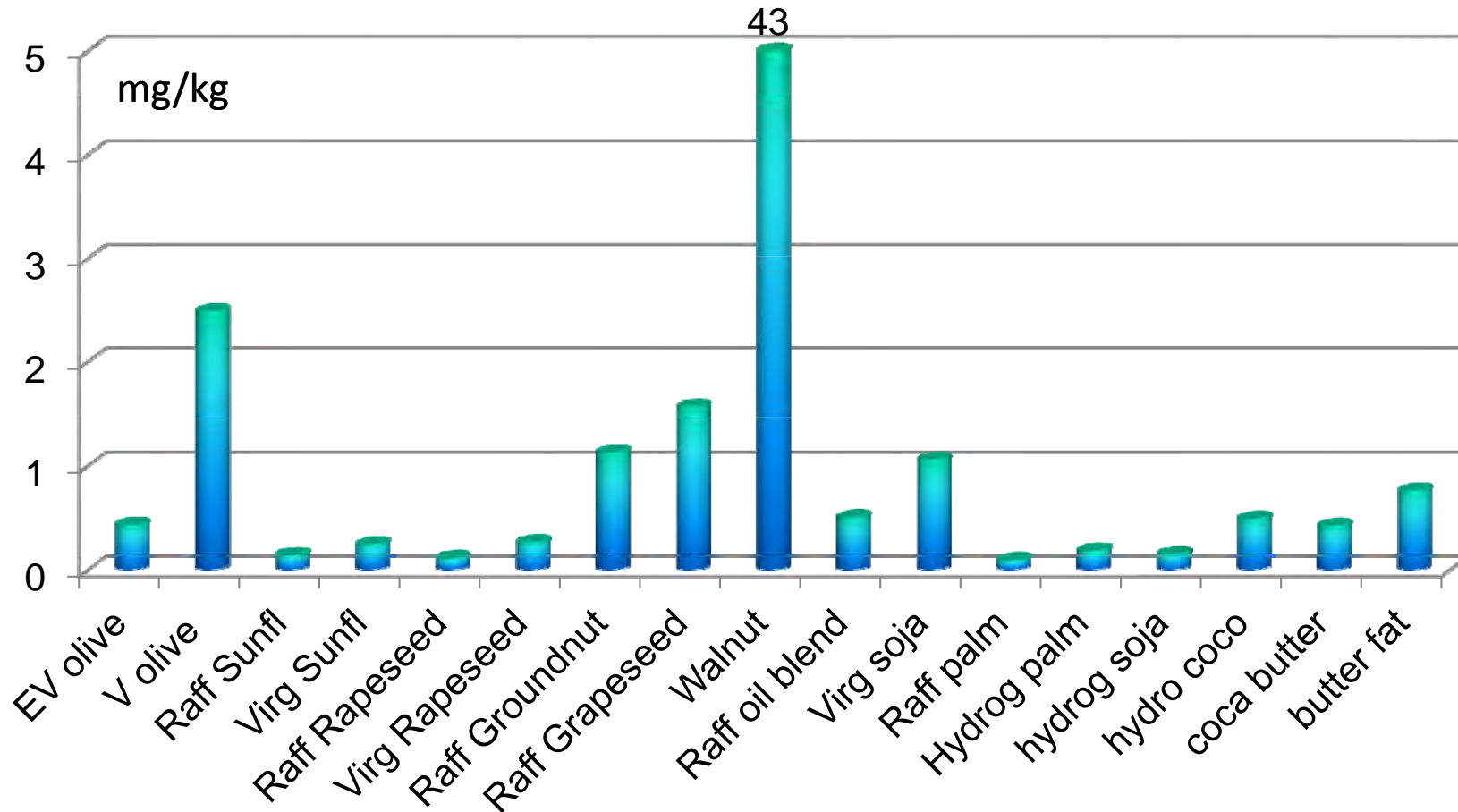
m/z 111 (adipates)  
m/z 149 (phthalates)



## Advantages of the method :

- ✓ No contamination, no solvent
- ✓ Rapid analysis (45 min)
- ✓ Sensitive LOQ < 0,1 mg/kg (excepted DINP & DIDP)

# DEHP in oils & fats



ITERG data, 2009

# Conclusions

- Research of contaminants is part of multiple controls conducted by fat and oil industry to fulfill the EC regulation n°1881/2006.
- In the absence of regulation, the detection of contaminants must be addressed in partnership with authorities according to the toxicity of molecules.
- Risks are rather limited due to the efficient elimination during oil-refining steps
- However some contaminants can be formed during the production process of vegetable oils such as esters of 3-MCPD & esters of glycidol.



**A special thanks to...**



## **ITERG Analysis Department team**