HEALTH AND ORGANOLEPTIC RISKS FROM BISPHENOL A LEACHED FROM EPOXY RESINS

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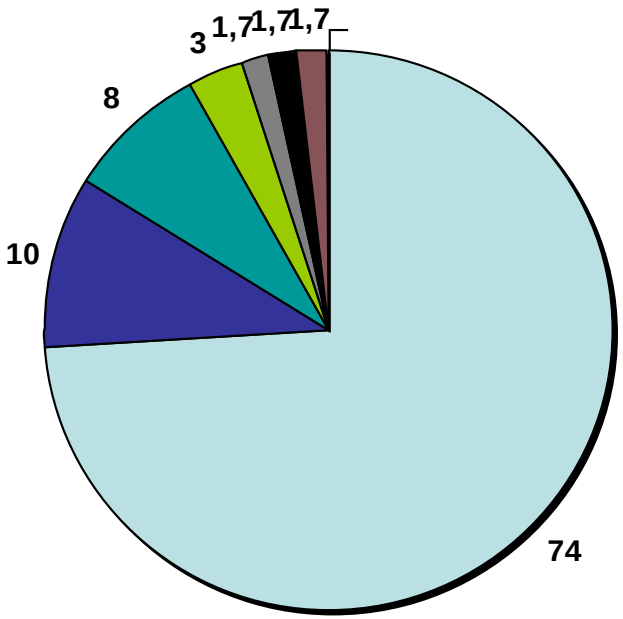
ENTREPRISE

CONTEXT



Examination of the lists of approved coatings in France and USA, indicates that epoxies still represent about 50% of approved coatings in 2010. Also used in UK, Spain and Germany

CONTEXT

A taste-and odour episode that occurred in the Bordeaux area (2008, 2011) showed that a 10 year old epoxy lining (ClO2) had completely failed and released bisphenol A, leading to chlorinated phenols and anisoles with taste-and odour complaints-Pink colour also observed

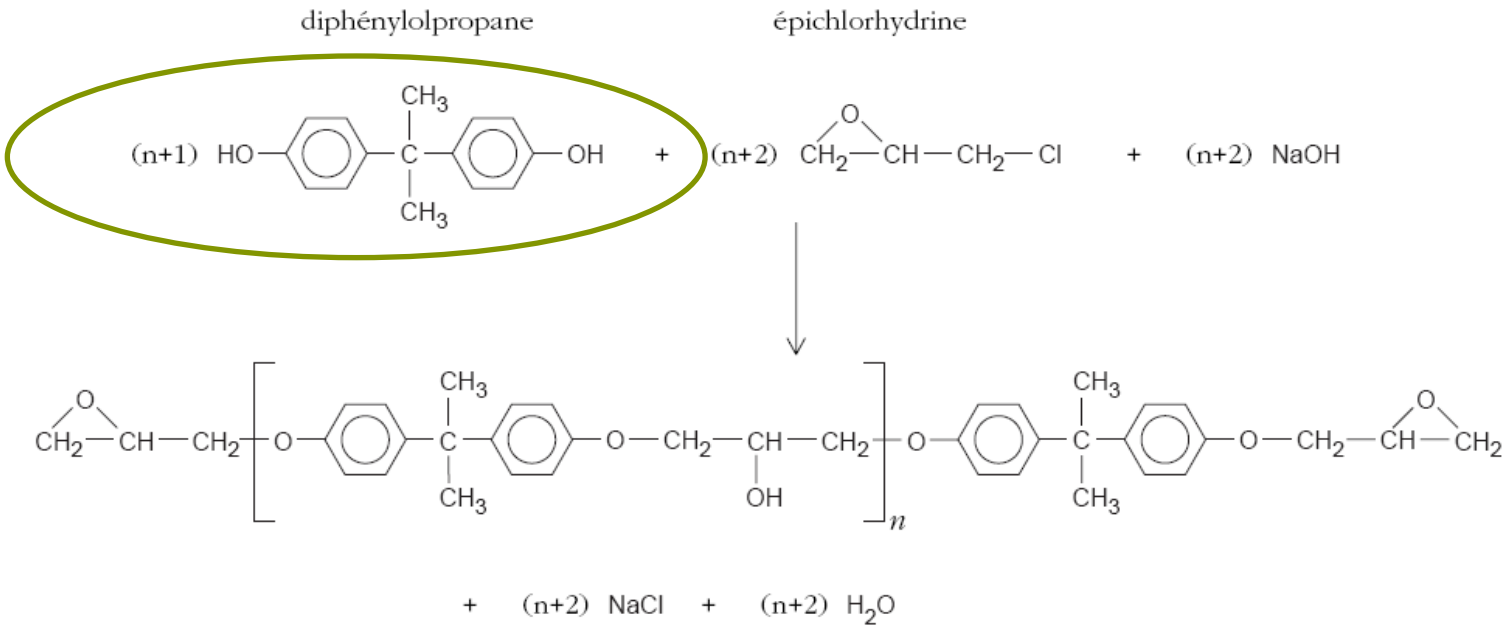
CONTEXT

Epoxies are produced by reaction of bisphenol A with epichlorohydrin in the presence of sodium hydroxyde

Bisphénol A

Epichlorydrine

Soude



If n=1, compound is called BADGE

Bardonnet P., *Techniques de l'ingénieur : traitement des plastiques*, **2009,** A3 465

CONTEXT

➢ Organoleptic risk

BPA

2,4,6 Trichlorophenol

2,4,6 Trichloroanisol (musty)

Chlorination of bisphenol A in aqueous media: formation of chlorinated bisphenol A congeners and degradation to chlorinated phenolic compounds

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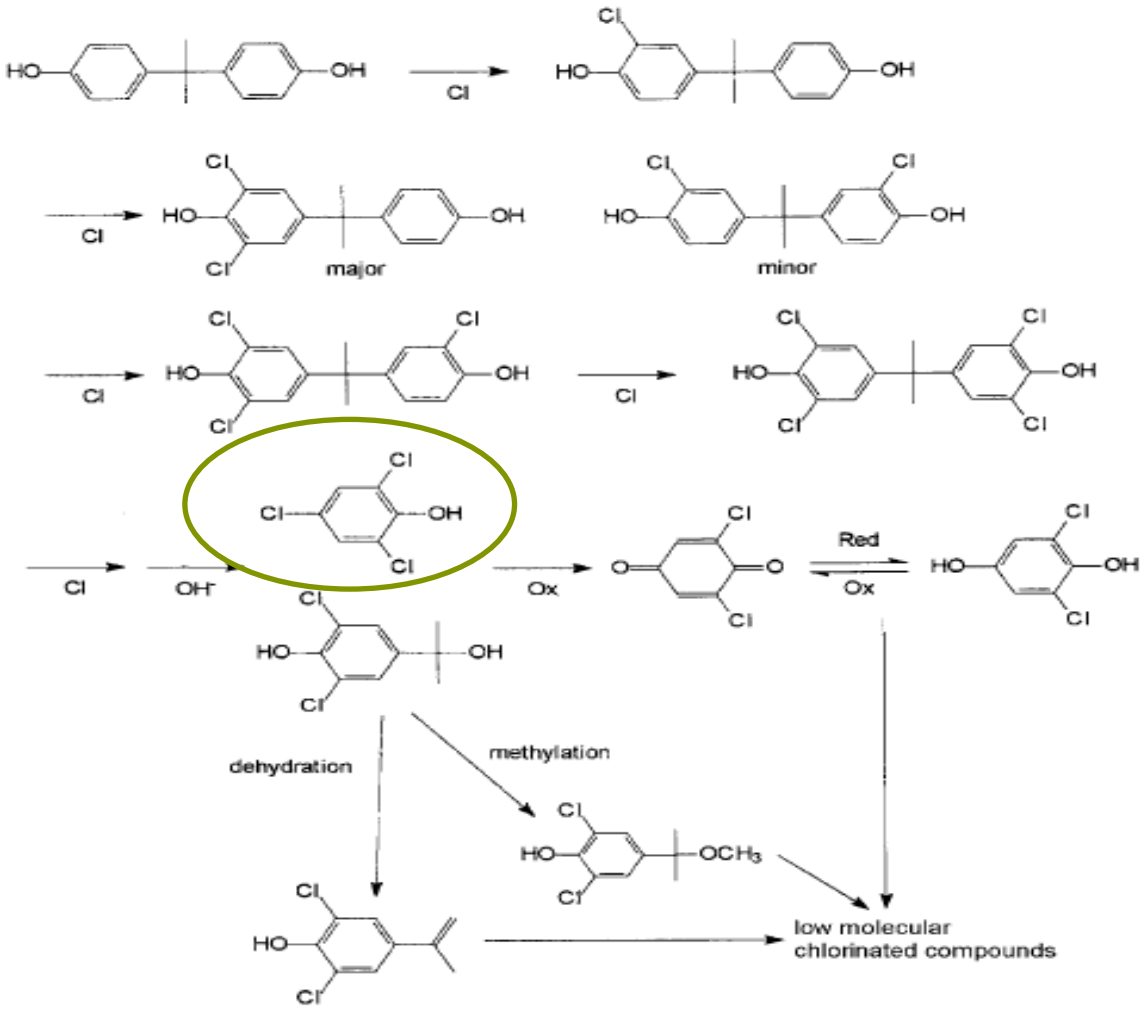


Fig. 5. Presumed chlorination reaction scheme of BPA.

[3]Yamamoto, T., Yasuhara, A. 2002. Chlorination of bisphenol A in aqueous media: formation of chlorinated bisphenol A congeners and degradation to chlorinated phenolic compounds. *Chemosphere,* 46, 1215-1223

CONTEXT

➢ Health risk

The discovery that baby drinking bottles can leach bisphenol A, a known endocrine disruptor, has raised an intense public issue in the US then in Europe. Bisphenol A has been forbidden for this use in various countries (Canada, France: june 2010)

Bisphenol A, a High Production volume chemical (2.2 million tons in 2003) is primarily used for the synthesis of polycarbonate and epoxy polymers.

Public attention has been focused on the release of bisphenol A by baby bottles and food cans. Not aware of bisphenol A polymers introduced in drinking water distribution systems.

Lots of new publications indicate that BPA has effects at low doses, including on prostate weight, obesity, childhood behaviour

New Anses report recognizes effects of BPA on animals and suspects effects on humans, even at low doses.

In 2015 a French rule stopped the bisphenol A in all products for food contact

OBJECTIVES

- **Study the leaching of bisphenol A, bisphenol F and other organics from 3 new epoxies approved in France, Spain, UK and the USA**
- **Check that initial contact period does not expose consumer to high levels of BPA**
- **Carry out analytical campaigns at real sites with epoxies (storage tanks and rehabilitated pipes)**

ANALYTICAL METHOD

In situ acetylation of phenols followed by SBSE (Stir Bar Sorptive Extraction)-thermal desorption-GC/MS

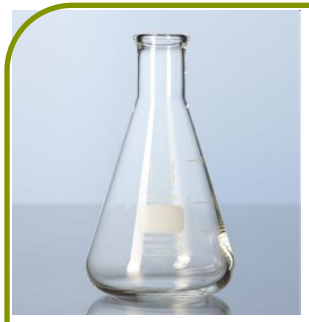
Instumentation :

GC Agilent 7890
RX i 5MS Restek Colum
Acquisition mode : Single Ion Monitoring (SIM)

The Stir-bar is then thermally desorbed into a

heated GC injection port connected to a MS detector

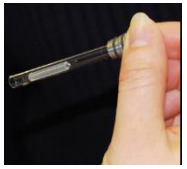
SAMPLE PREPARATION



- Add 2 g K_2CO_3
- 100 ml of sample + IS

1 ml acetic anhydre (Ac_2O)

- Add stir bar and agitate at 550 rpm during 1 hour

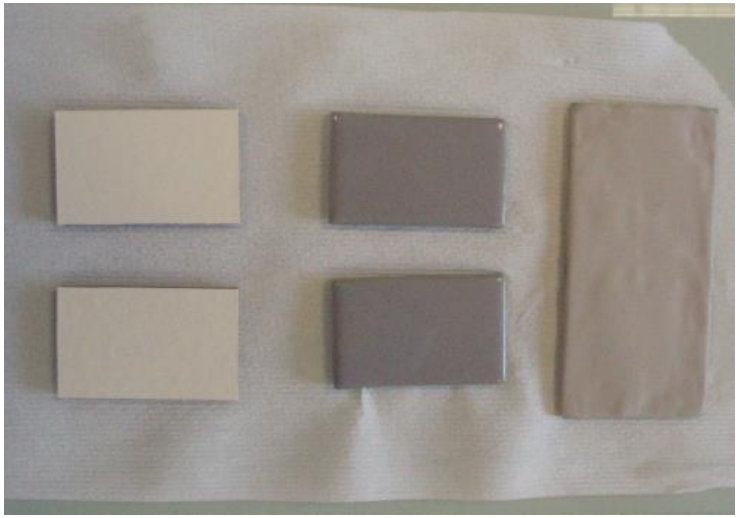


- Dry stir bar with paper and desorb

Composés	Fragment 1 (masse)	Fragment 2 (masse)
PCP C13	272	
2 ChloroPhénol	128	130
3 Chlorophénol	128	130
4 ChloroPhénol	128	130
2 isopropylphénol	121	136
3 isopropylphénol	121	136
4 isopropylphénol	121	136
2,6 Dichlorophénol	162	164
2,4 et 2,5 Dichlorophénol	162	164
3,5 Dichlorophénol	162	164
2,3 Dichlorophénol	162	164
3,4 Dichlorophénol	162	164
2,4,6 trichlorophénol	196	160
2,3,6 trichlorophénol	196	160
2,3,5 trichlorophénol	196	160
2,4,5 trichlorophénol	196	160
2,3,4 trichlorophénol	196	160
3,4,5 trichlorophénol	196	160
BPA C13	225	
Bisphénol F	200	242
Bisphénol A	213	228

LoQ : 10ng/L

IMMERSION TEST
PRELIMINARY TEST



- **Surface/Volume ratio:**

- **E1 : 50 cm^2/l , 1 test panel in 1.3 L**
- **E2 and E3 : 40 cm^2/l 2 test panels in 1.2 L**

- **contact time : 24 h ± 1 h**
- **immersion T° : 21 ° C ± 2° C**

- **Static condition, protected from light.**

After 24 h of contact,

Sampling of several aliquots :

Determination of chlorine residual : 10 mL

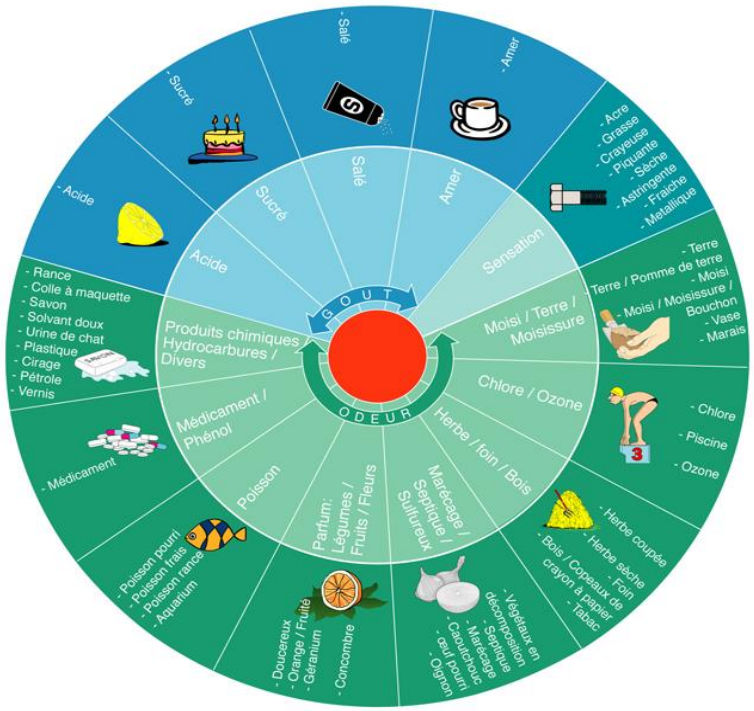
- **SBSE + GC/MS analysis (modes Full Scan et SIM) : 100 mL**

• **organic profile : liquid-liquid extraction 1 L with CH_2Cl_2**

Flavor Profile Analysis : 1 L

Romero, J. ; Ventura, F. ; Gomez, M. *Journal of Chromatographic Science,* **2002,** *40,* 191-197
Bae Jeong,J.H.; Lee, S.J. *Water Science and Technology,* **2002,** *46,* 11-12, 381-387

FLAVOR PROFILE ANALYSIS RESULTS



LA ROUE DES GOÛTS ET DES ODEURS
(M. Suffet, A. Bruchet et D. Khiari)

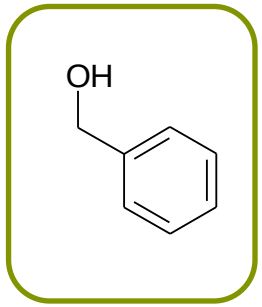
Objective : **Determine the organoleptic characteristics of contact water (taste and odour)**

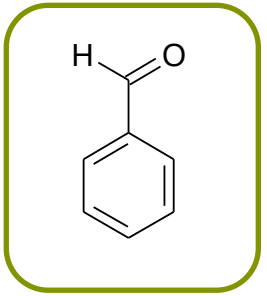
- **Jury of five panellists**
- **FPA Method :**
  Odor at 45 ° C and taste at 25 ° C
- **Prior dechlorination of waters with L-ascorbic acid at 5,0 g/l**

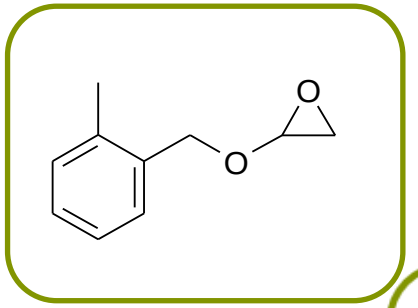
	Taste		Odor	
Epoxy	No chlorine	With chlorine	No chlorine	With chlorine
E1	**Hydrocarbon** (6)	**Chemical** (4)	**Hydrocarbon** (6)	**Chemical** (4)
		(plastic, varnish)		**(plastic, varnish)**
E2	-	**Chemical** (2)	-	-
E3	**Biogas** (7)	**Plastic-chemical** (6)	**Biogas** (5)	**Chemical**(5)
	Hydrocarbon		**Hydrocarbon**	**(paint, varnish)**

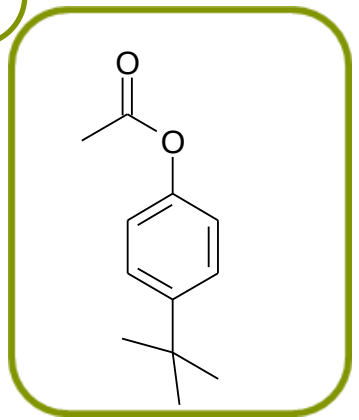
ORGANIC PROFIL

Liste des composés relargués	J1 (µg/L)	J3 (µg/L)	J1 (µg/L)	J3 (µg/L)
Epoxy E1	**Sans Chlore**		**Avec Chlore**	
Benzaldéhyde	Cet échantillon n'a pas pu être analysé		2	-
N,N- Diethylcarbamicchloride			0,5	-
Dibutyl Phtalate			2,4	0,2
Benzophénone		0,2	0,4	0,4
Epoxy E2	**Sans Chlore**		**Avec Chlore**	
Alcool Benzylique	140	1	96	87
O-cresolglycidylether	1,4	0,2	-	-
Epoxy E3	**Sans Chlore**		**Avec Chlore**	
Benzaldéhyde	3	Aucun composé visible	2,8	-
Diethylèneglycol	1,1		-	-
Alcool Benzylique	12		8,1	0,97
Methoxy Phénol	6,8		1,2	
Tert-Butyl Phénol	0,6		0,2	-
Vanilline	9,8		1,4	-
Chlorovanilline			2,2	-
Diethyl Phtalate	0,9		7,1	1,4
Propane, 1-(dodecyloxy)-2,3-epoxy	2,9		2,3	-
4-Hydroxy-3,5-dimethoxybenzaldéhyde	1,3		-	-
Benzophénone	0,8		1,4	-
N,N- Diethylcarbamicchloride	-	-	-	1,8

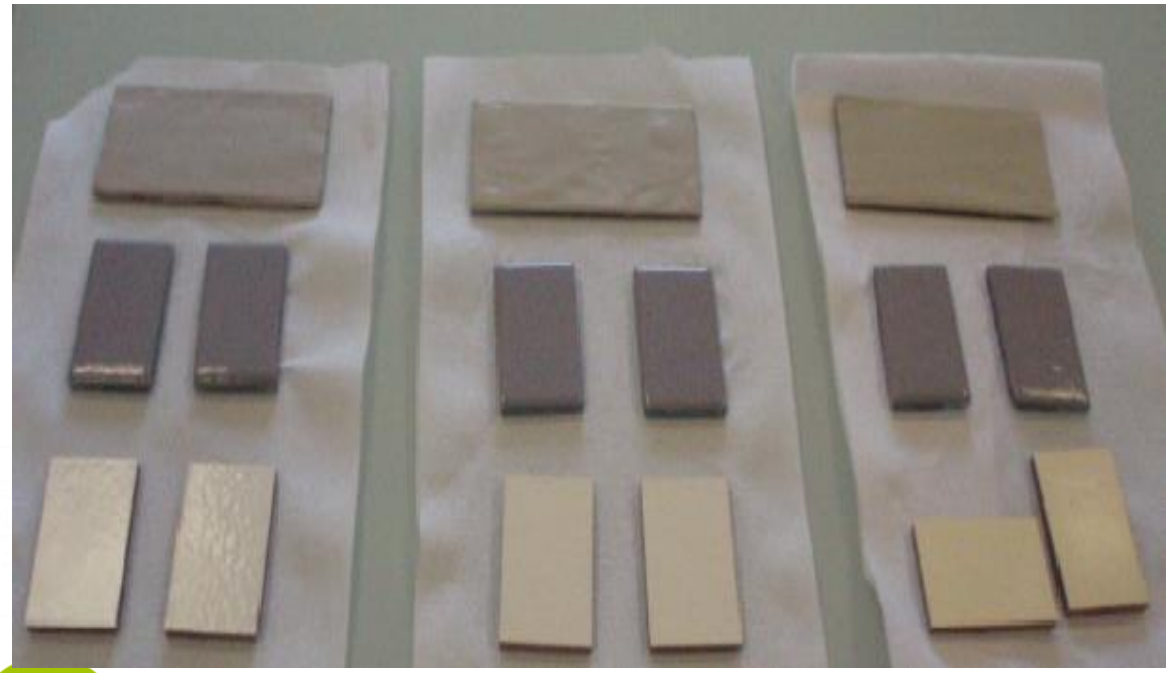








IMMERSION TEST



Immersion test :

March –August

S/V 40-50 cm2/L

Contact time 24 h, at 20° C

Series 1: Without disinfectant

Series 2: 0,5 mg/l Cl

Series 3: 0,25 mg/l ClO_2


2 MODELES DE TITRE
Modèle 1 : PHOTO A CHANGER DANS LE MASQUE
Modèle 2 : FOND VERT voir DIAPO SUIVANTE
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FIELD SAMPLING: TANKS

27 tanks sampled in Paris area (CRY, SEVESC and ESP), from 60 to 2000 m3, most recent renovation: 2010

	RESERVOIRS DU CRY							
RESERVOIRS	**R12**	**R13**	**R14**	**R15**	**R16**	**R17**	**R18**	**R19**
Volume (m3)	**200**	**500**	**2000**	**800**	**1000**	**4500**	**1100**	**1100**
Cl total (mg/l)	**0,09**	**0,17**	**0,31**	**0,18**	**0,24**	**0,4**	**0,4**	**0,39**
Cl libre (mg/l)	**0,05**	**0,12**	**0,19**	**0,11**	**0,2**	**0,35**	**0,4**	**0,37**
Date de pose	-			**nov-10**	-			
	Concentration (ng/l)							
2 ChloroPhénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
3 Chlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
4 ChloroPhénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
2 isopropylphénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
3 isopropylphénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
4 isopropylphénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
2,6 Dichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
2,4 2,5 Dichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
3,5 Dichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
2,3 Dichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
3,4 Dichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
2,4,6 trichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
2,3,6 trichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
2,3,5 trichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
2,4,5 trichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
2,3,4 trichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	**13**	<LoQ
3,4,5 trichlorophénol	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Bisphénol F	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Bisphénol A	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ

No bisphenols and no degradation by-products detected

FIELD SAMPLING: PIPES

20 pipes from the Bordeaux area. Selection of results

Pipe N°	119	19	38	45	31	20	99
Diameter (mm)	150	200	100	100	100	150	100
Rehabilitation date	1996	1998	1992	2003	1992	1999	2000
Flow	low	No flow	low	medium	Dead end		low
Chlorine residual (free)	0.09	0,06	0,03	0,04	0,04	0,04	0,04
Bisphenol F	**100**	**114**	**134**	**1666**	**38**	**1050**	**25**
Bisphenol A	**17**	**31**	**90**	**<LoQ**	**62**	**151**	**421**

-Much higher leaching of BPA and BPF

-No apparent link with pipe and water quality characteristics

-Possible reasons: high S/V, long contact times, **conditions of application**, accelerated ageing with Cl02

CONCLUSION

- Initial leaching of BPA by new epoxies is low. However one epoxy showed increased leaching increase during first 4 months : are official approval tests (1 week of immersion) adapted?
- Laboratory and field tests indicate that there is no reason to stop using epoxies in storage tanks where S/V <50 cm2/l (initial check of BPA is however recommended)
- On the other hand, the use of epoxies for pipes rehabilitation should be discontinued
- For existing epoxy-coated pipes, maintaining enough chlorine residual to destroy bisphenol A is necessary
- Pending for more information, use of ClO2 in the presence of epoxies is not recommended
- 2,4,6-trichlorophenol frequently detected when epoxy is in contact with chlorinated water and hence represents an organoleptic threat

Thank you