3rd Stir Bar Sorptive Extraction

Technical Meeting, Paris

RESEARCH & INNOVATION

Iodinated phenols monitoring by SBSE-GC/MS

Faten BELHAJ-KAABI, Delphine BOURDIN and Pasacl ROCHE

Veolia Research & Innovation

Outlines

Fate of iodine during water disinfection

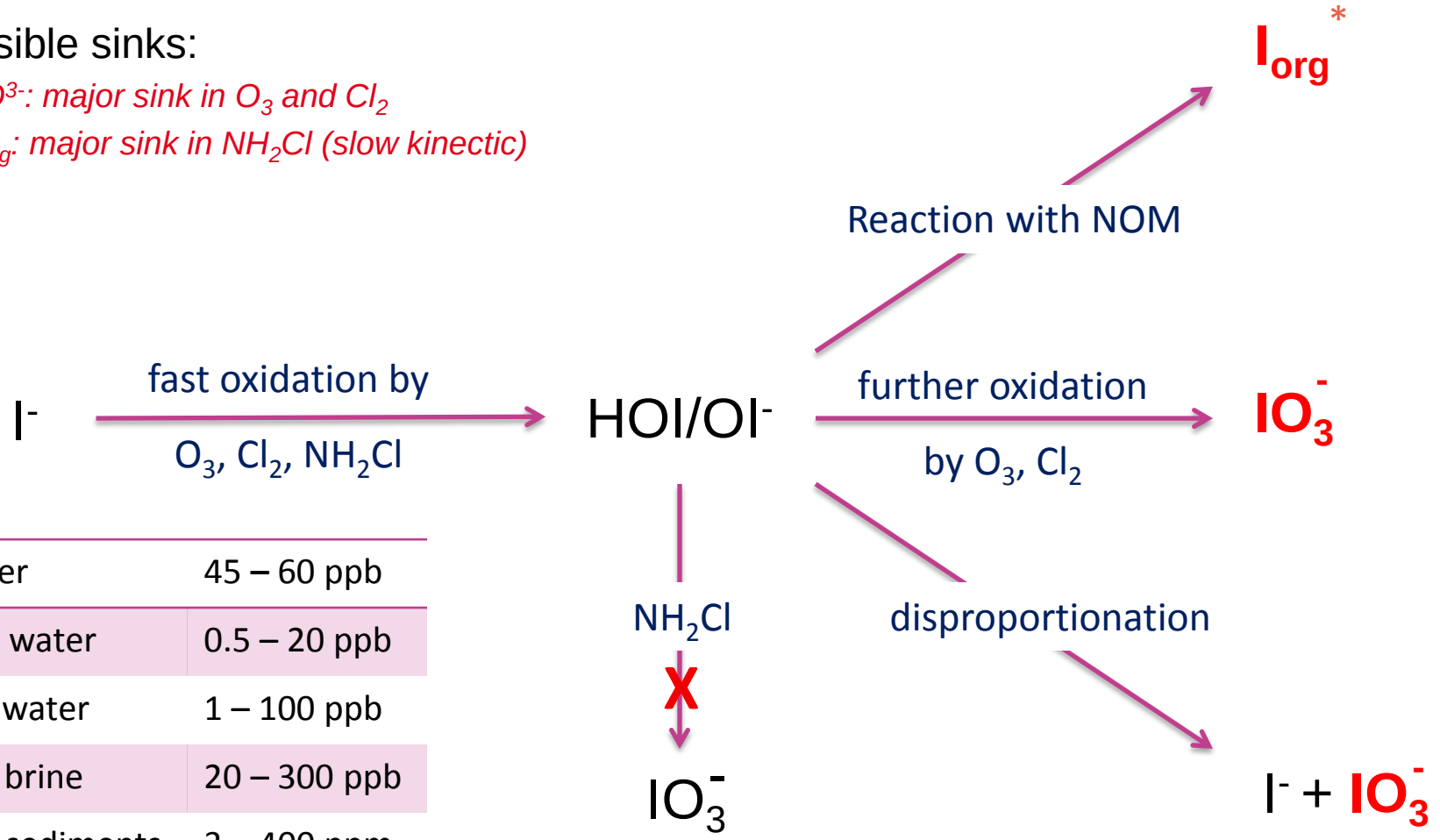
Iodinated halophenols monitoring at low ppt level

Application to natural and model waters

Conclusions & outlooks

Fate of iodine during oxidative processes

- Possible sinks:
  - *IO^{3-}: major sink in O_3 and Cl_2*
  - *I_{org}: major sink in NH_2Cl (slow kinectic)*

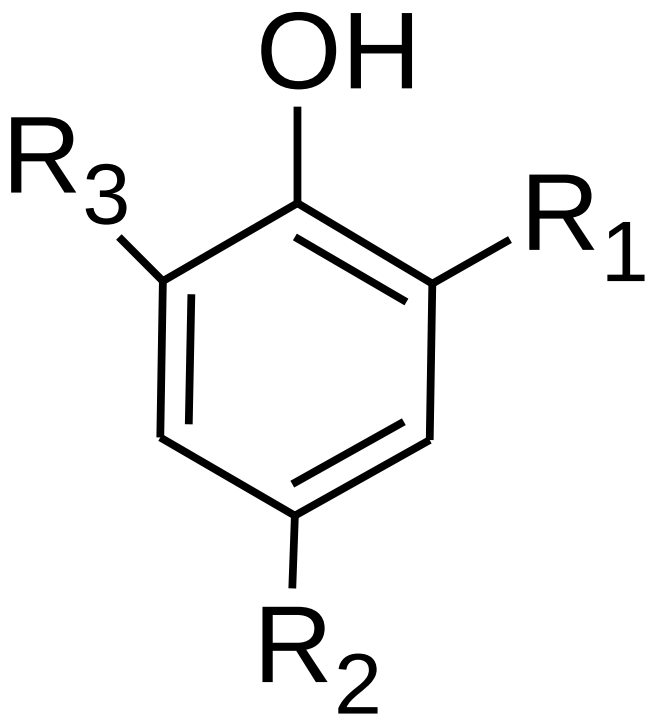


Seawater	45 – 60 ppb
Surface water	0.5 – 20 ppb
Groundwater	1 – 100 ppb
Oilfield brine	20 – 300 ppb
Marine sediments	3 – 400 ppm

* Bichsel and Von Gunten, *Environ. Sci. Technol*. **1999**, 33, 4040-4045

Iodinated phenols

- Electron donating capacity of the hydoxyl group
- Electrophilic regio-selective substitution with electrophiles (e.g., Cl^+, Br^+, I^+)
- *Orhto & para* substitution *(4 resonance structures vs meta: only 3)*



- ❖ **pKa:** 6 to 8.5
- ❖ **Organic Threshold Concentration :** 1 ppb
- ❖ **Descriptors:** Chemical, phenolic, medicinal
- ❖ **Ecotox:** LD50 triodophenol (fish) 1.2 ppm

- R1, R2 et R3 : H and/or halogen (I, Cl, Br)

Goals

- New analytical method for the of I-halophenols

  - ❖ 23 congeners of interest
  - ❖ Only 9 available (5 via outsourcing in USA)
  - ❖ Iodophenol mono, di et trisubstituted
  - ❖ 3 congeners I-Cl-Br

- SBSE-GC/MS
- Study the occurrence of I-halophenols during oxidative drinking water treatment

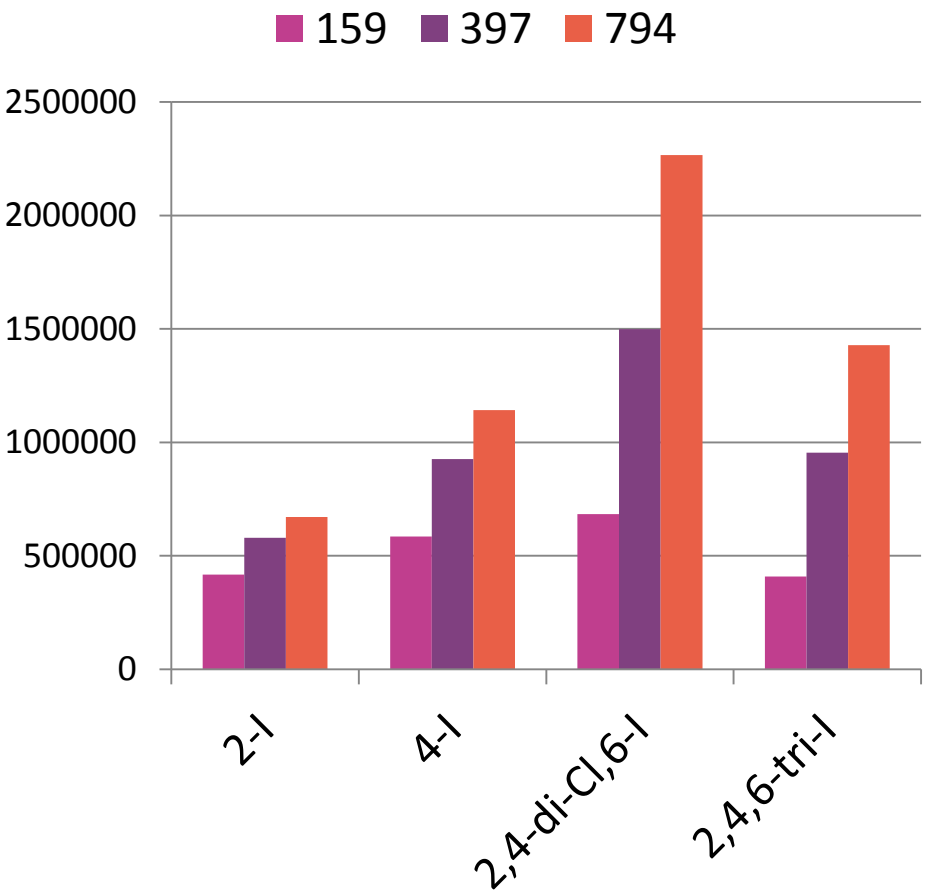
Iodinated phenols monotoring

SBSE optimization

- Extraction
  - *Chemical modification: Acylation (acetic anhydride + K_2CO_3)*
  - *Phase ratio: sample volume/PDMS volume (fixed PDMS volume 126 µL)*
  - *Organic modifier*
  - *Extraction time*
  - *Multiple extraction: multishot*
- Thermal desorption-GC/MS
  - *Desorption temperature*
  - *Desorption flow*
  - *Desorption time*
  - *Cryofocalisation temperature*
- Conditionning and re-use of stir bars: internal procedure

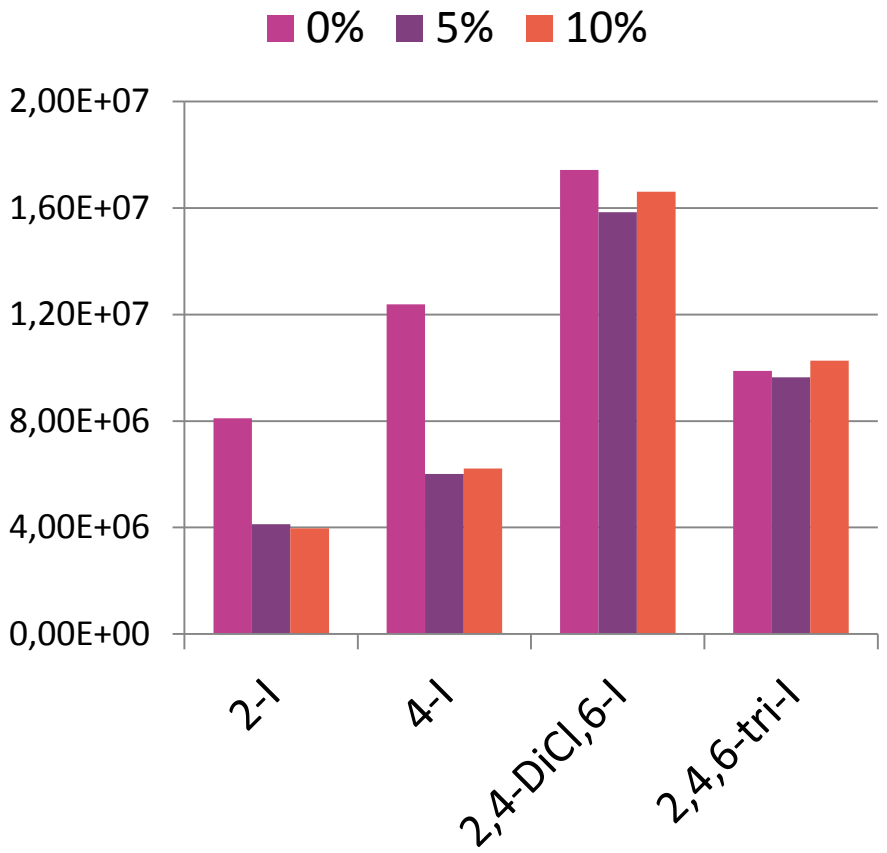
SBSE optimization: extraction

Phases ratio (β)



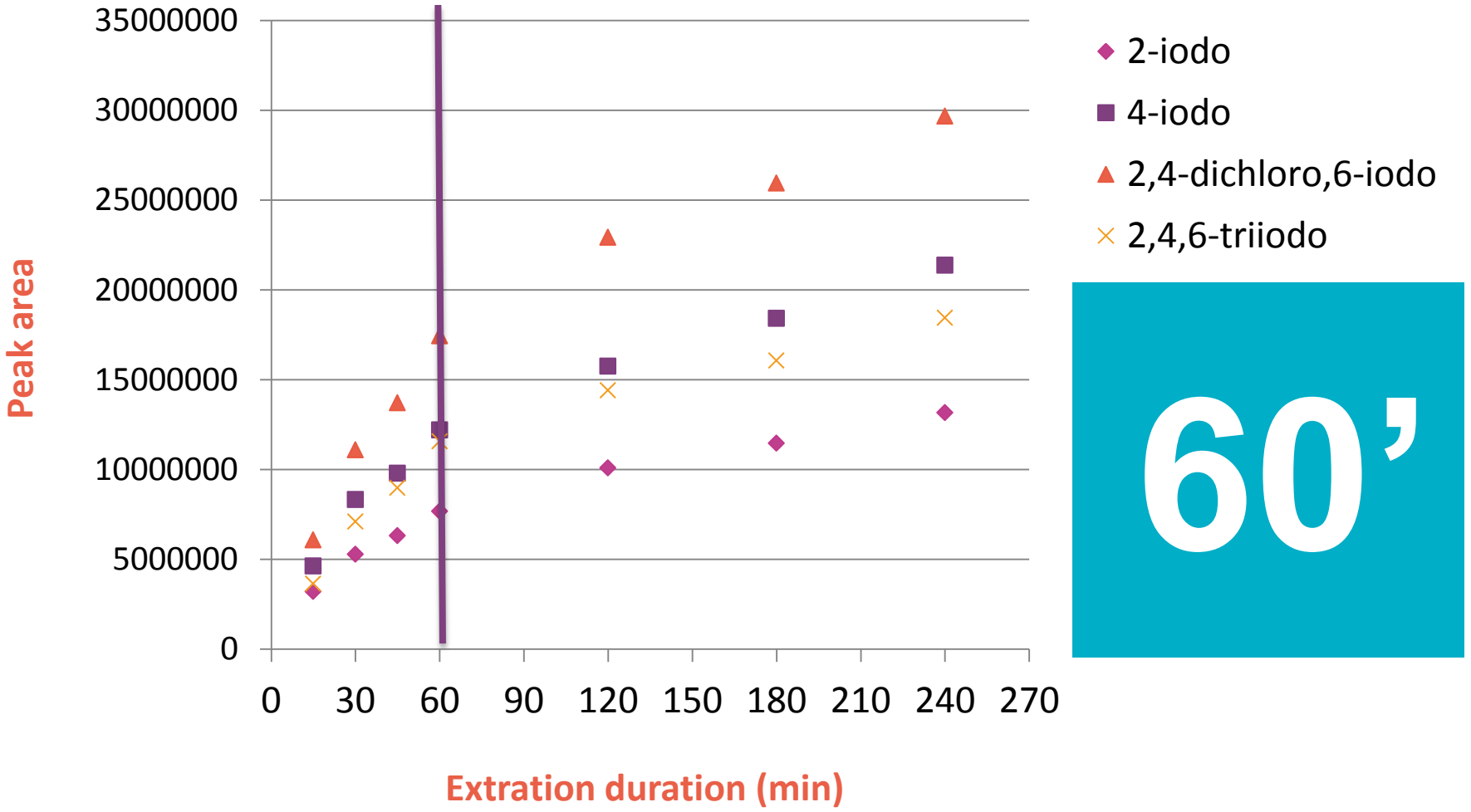
100 mL sample

Organic mofier content (MeOH)

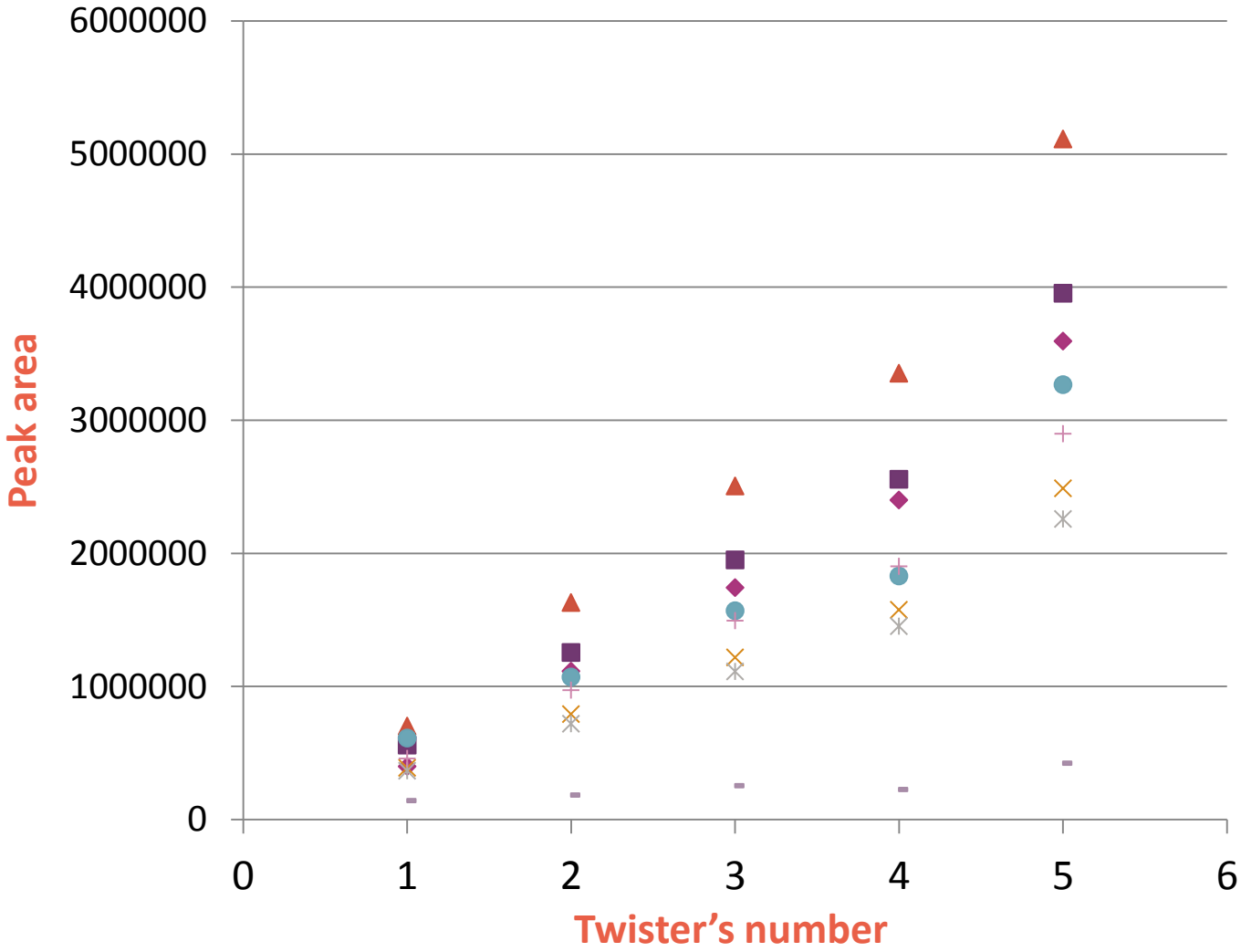


no organic modifier

SBSE optimization: extraction

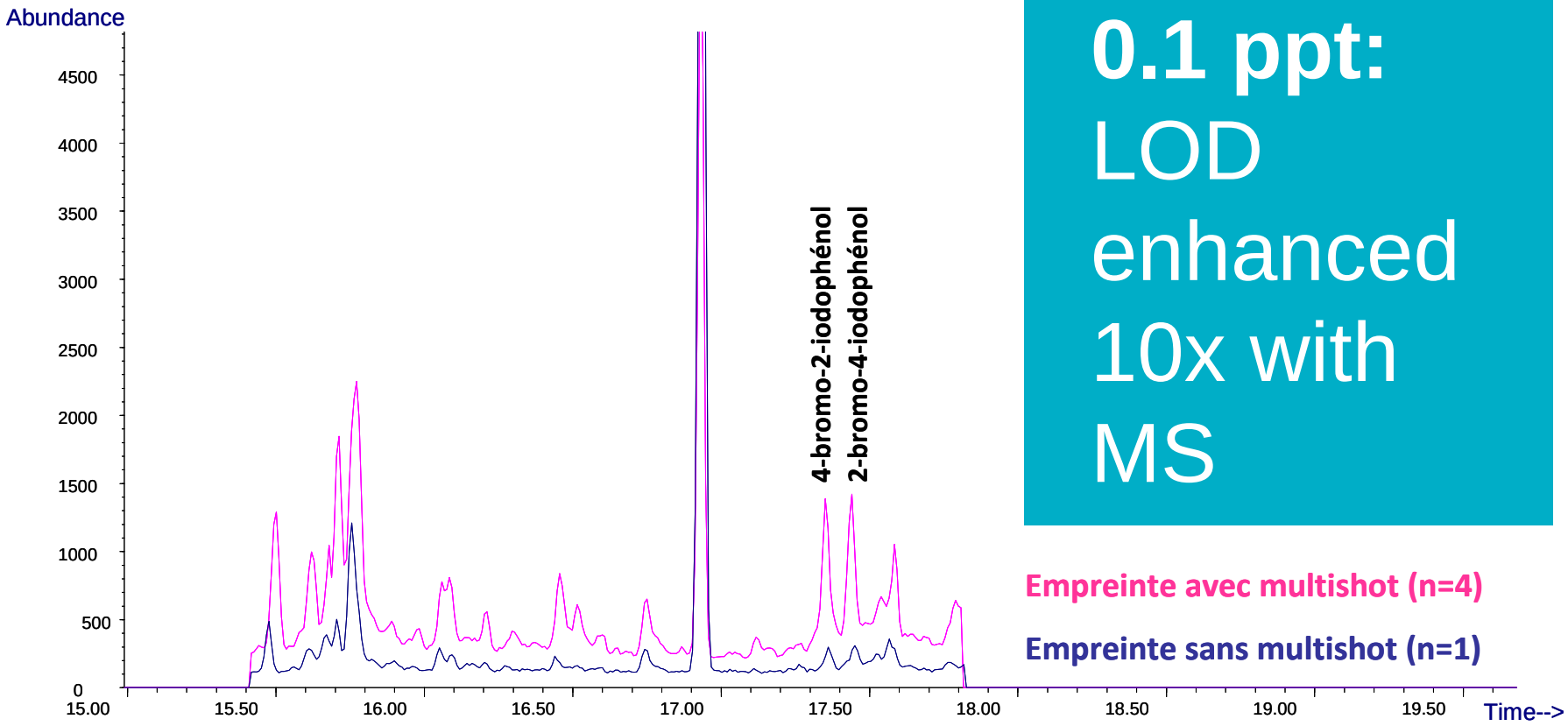


SBSE optimization: multishot



4 shots

SBSE optimization: Sensibility enhancement with multishot



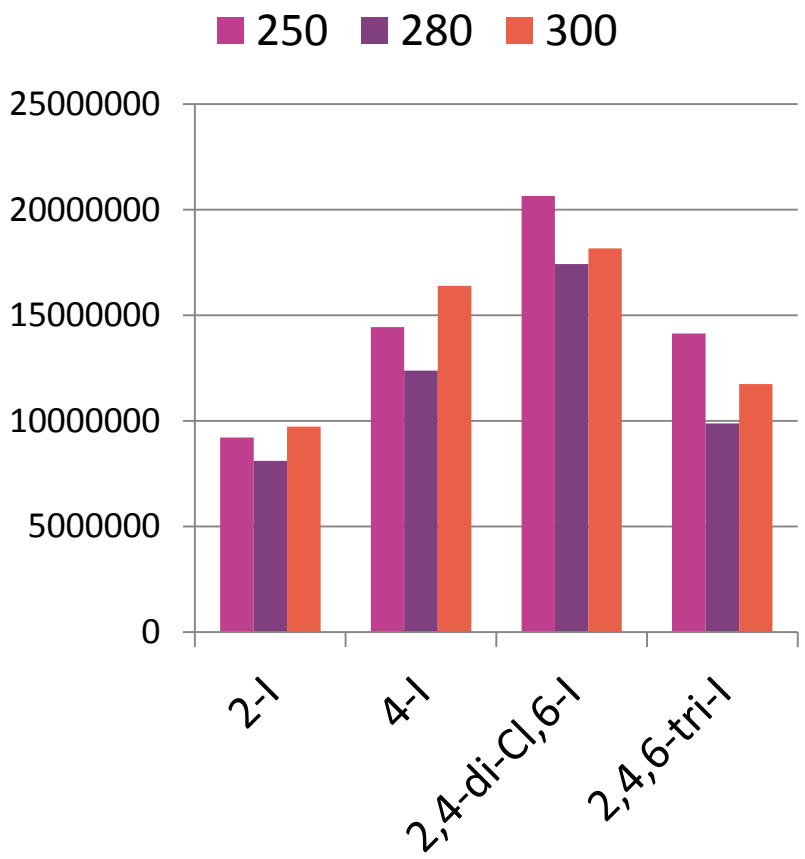
0.1 ppt: LOD enhanced 10x with MS

Ion m/z 298 with & without multishot

Standard mixture of iodinated phenols @ **0,1 ppt level**

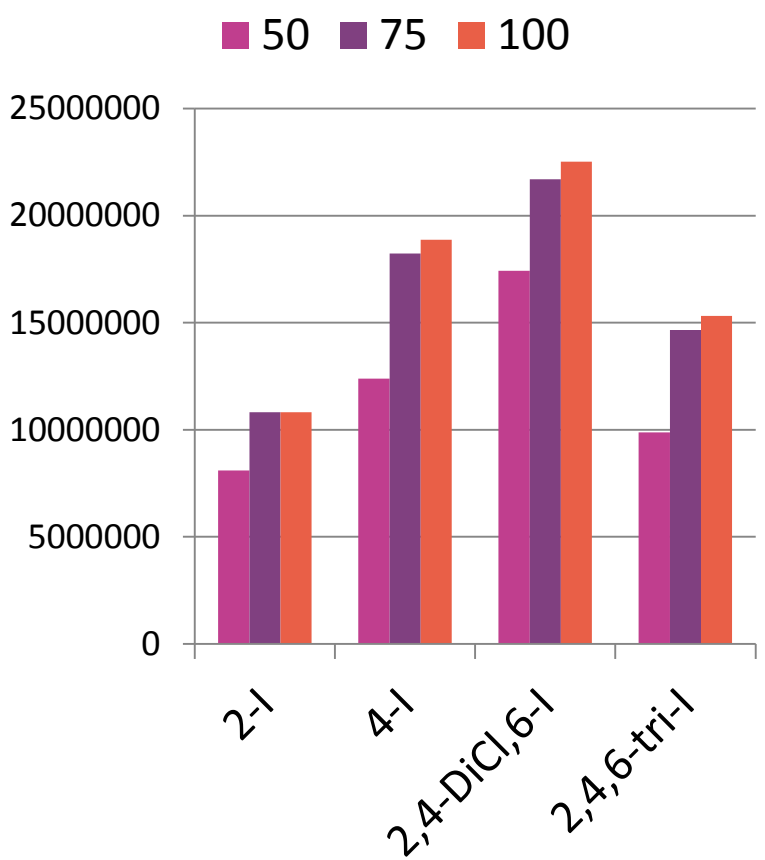
SBSE optimization: thermal desorption

Desorption temperature



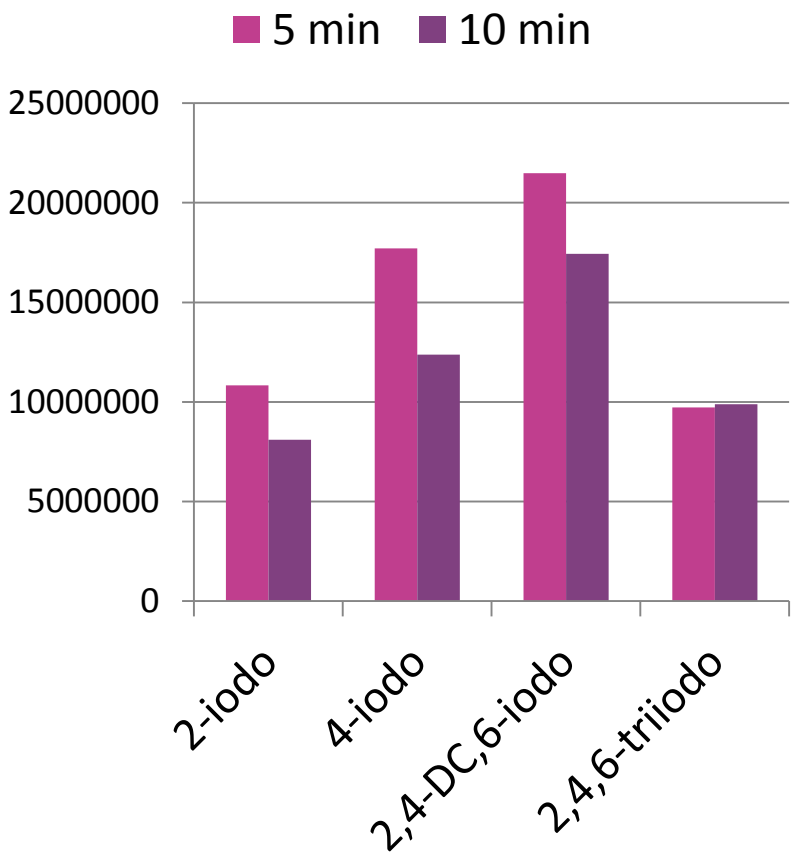
250 °C
desorption temperature

Desorption flow



75 mL/min
desorption flow

Desorption time



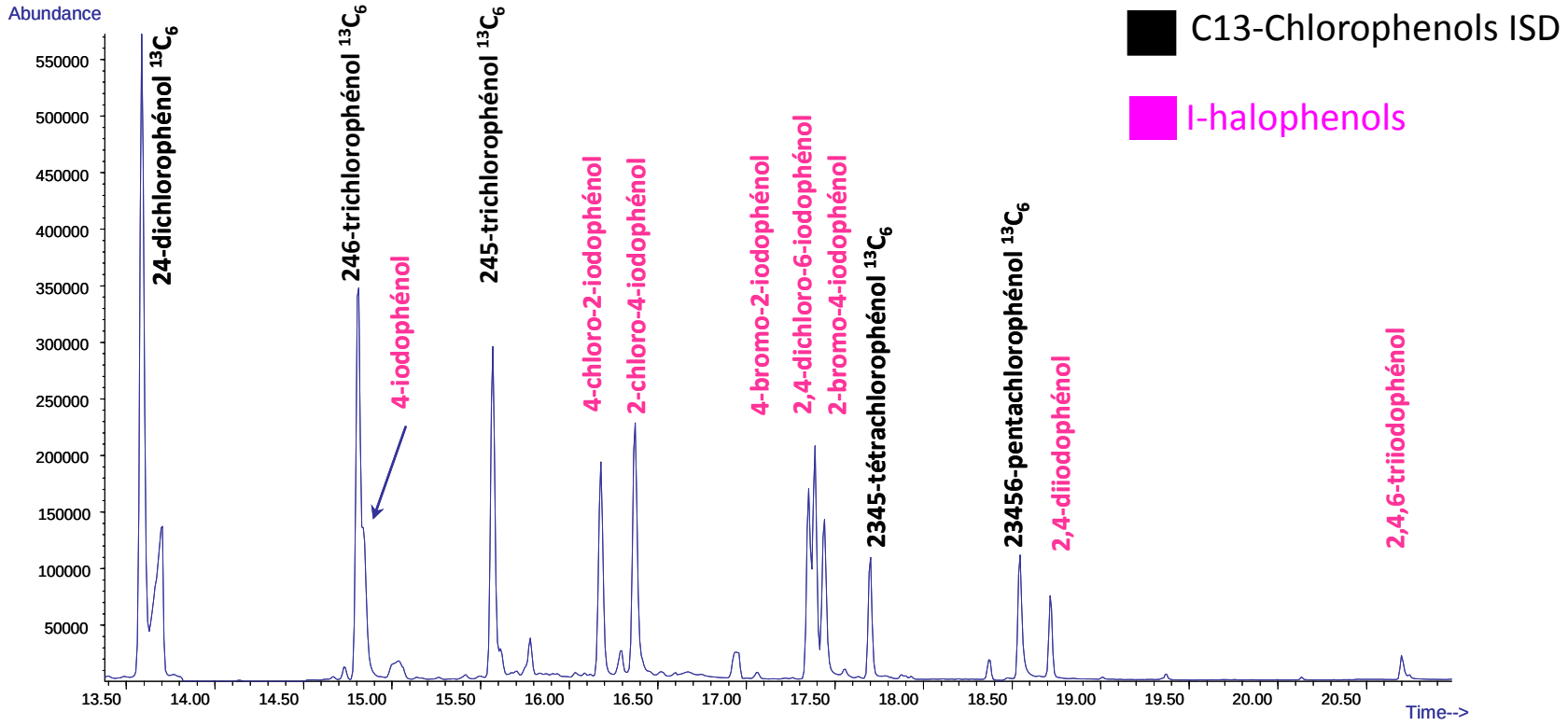
5 min desorption flow

-75°C cryofocalisation

SBSE optimized conditions

Step	Parameter	Optimized Value
Extraction	PDMS volume	**127 µL (20 mmx1 mm e.f.)**
	Sample volume	To be optimized
	Organic modifier (%)	no
	Chemical modification	Derivatisation with acetic anhydride
	Extraction time (min)	60 min
Desorption	Desorption temperature	250 °C
	Desorption duration (min)	**5 min**
	Flow rate	**75 mL/min**
	Cryofocalisation temperature	-50 °C

Chromatogramme of the standard mixture

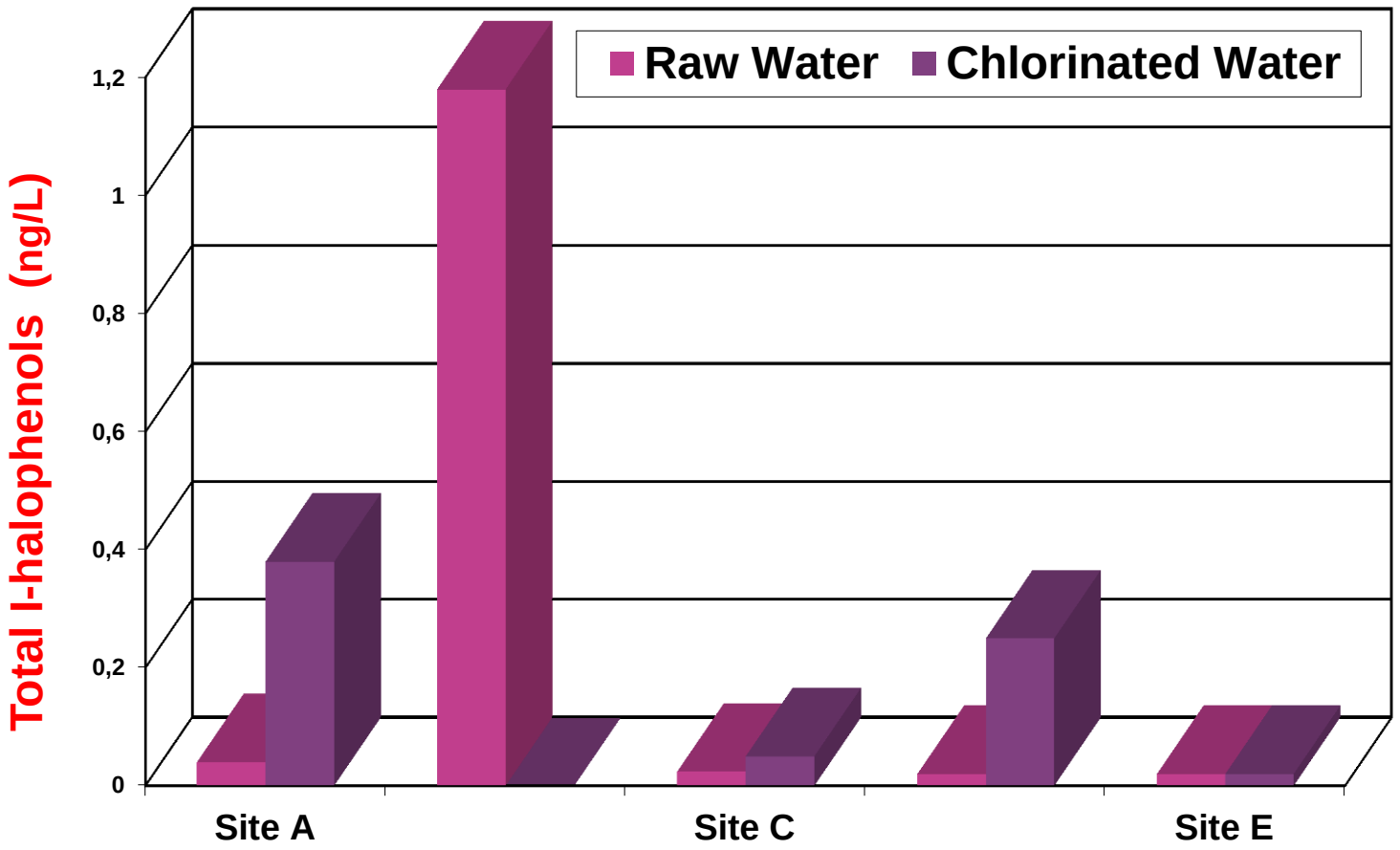


Standard mixture of iodinated phenols @ **10 ppt level multishot** (n=4)

Application to real and model waters

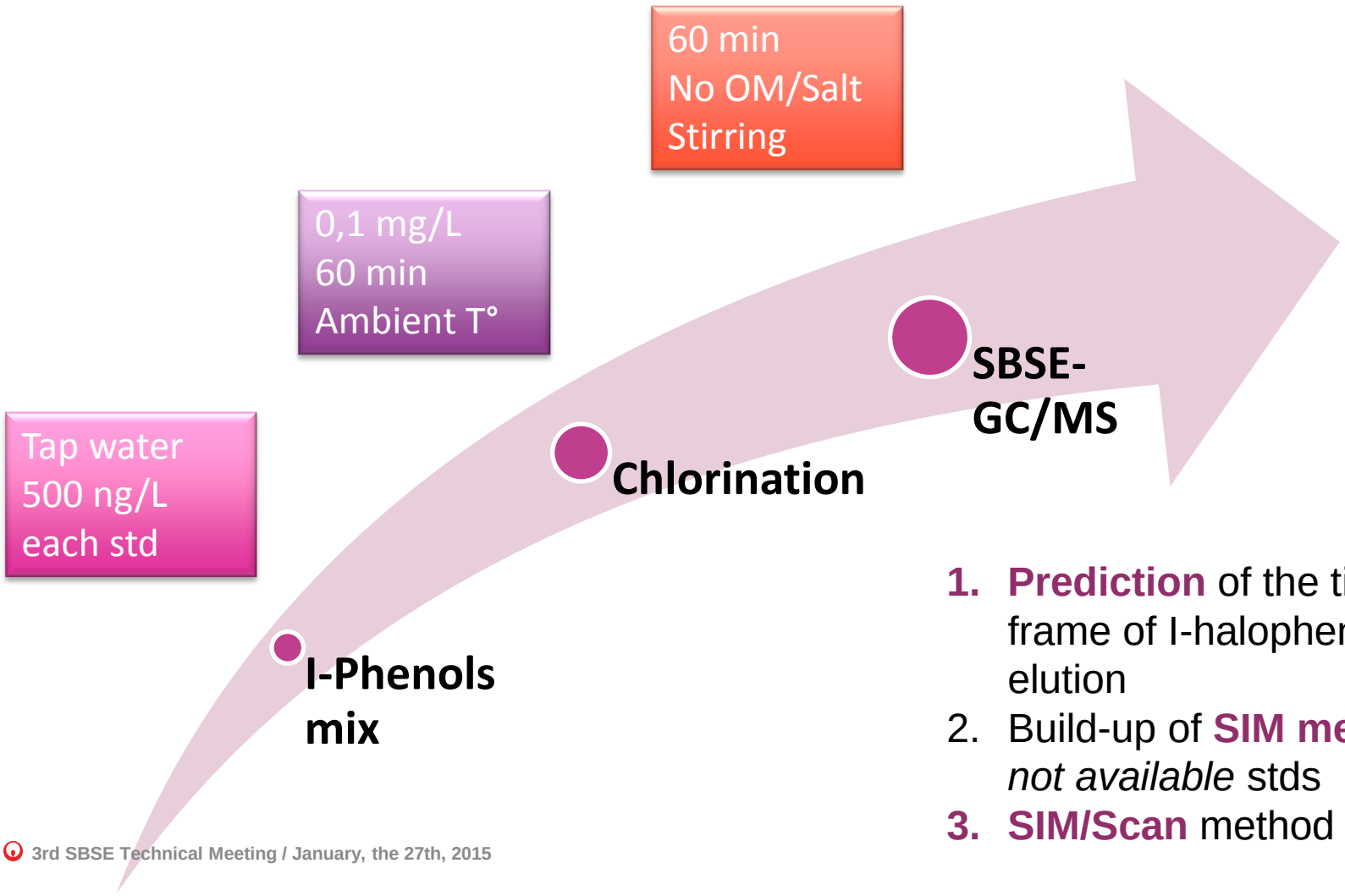
Subtitle

Fate of I-halophenols: coastal natural waters



Very low abundance of I-Halophenol
Occurrence below 1 ppt level

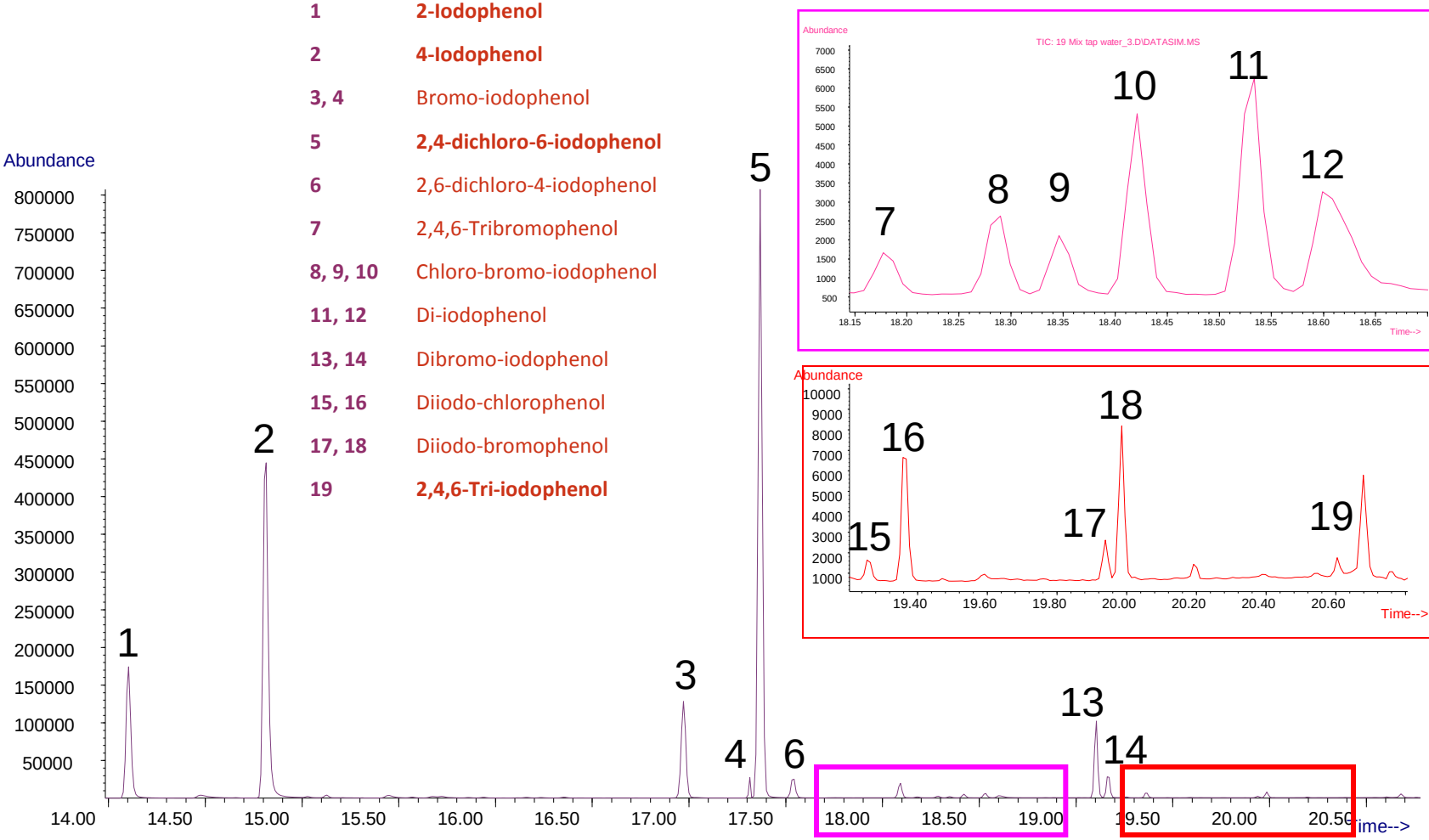
Synthesis of I-halophenols: principle



1. **Prediction** of the time frame of I-halophenol elution
2. Build-up of **SIM method** for *not available* stds
3. **SIM/Scan** method

Synthesis of I-halophenols: results

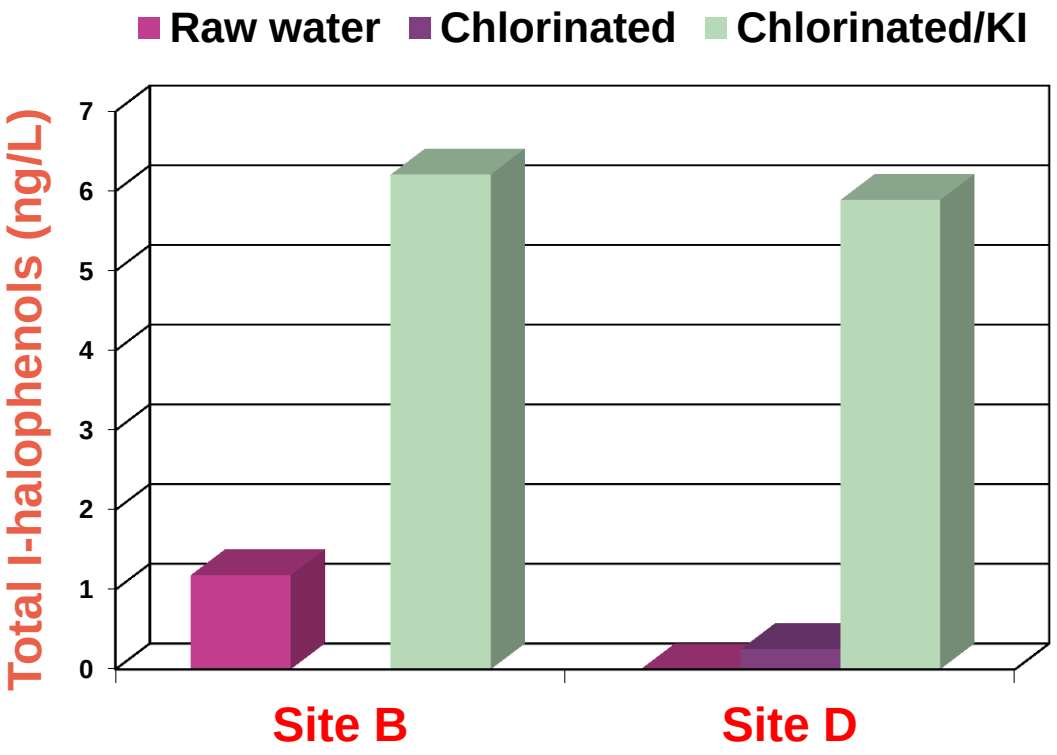
1	**2-Iodophenol**
2	**4-Iodophenol**
3, 4	Bromo-iodophenol
5	**2,4-dichloro-6-iodophenol**
6	2,6-dichloro-4-iodophenol
7	2,4,6-Tribromophenol
8, 9, 10	Chloro-bromo-iodophenol
11, 12	Di-iodophenol
13, 14	Dibromo-iodophenol
15, 16	Diiodo-chlorophenol
17, 18	Diiodo-bromophenol
19	**2,4,6-Tri-iodophenol**



Synthesis of I-halophenols: results

Pic N°	RT (min)	SIM (Isotopic ratio))	Formula	Compound
1 **2**	**14.123** **14.815**	**220, 262**	**C_6H_5OI**	**2-Iodophenol** **4-Iodophenol**
3 **4**	16.972 17.314	298 (100), 300 (98)	C_6H_4OIBr	Bromo-iodophenol
5	**17.368**	**288 (100), 290 (65), 292 (11)**	**$C_6H_3OICl_2$**	**2,4-Dichloro-6-iodophenol**
6	17.532	288 (100), 290 (60), 292 (10)	$C_6H_3OICl_2$	2,6-Dichloro-4-iodophenol
7	18.093	328(34), 330(100), 332(98), 334(32)	$C_6H_4OBr_3$	Tribomophenol
8 **9** **10**	18.290 18.346 18.421	332 (78), 334 (100), 336 (25)	$C_6H_3OIBrCl$	Chloro-bromo-iodophenol
11	18,533	346 (100)	$C_6H_4OI_2$	Di-iodophenol
12 **13** **14**	18,599 19.105 19.161	376 (51), 378 (100), 380 (49)	$C_6H_3OIBr_2$	Dibromo-iodophenol
15	19.368	380 (100), 382 (33)	$C_6H_3OI_2Cl$	Di-iodo-chlorophenol
16 **17**	19.939 19,986	424 (100), 426 (98)	$C_6H_3OI_2Br$	Di-iodo-bromophenol
(Scan)	**20.682**	**472**	**$C_6H_3OI_3$**	**2,4,6-Triiodophenol**

Fate of I-halophenols: model waters



COT	12.6 mg/L	3.2 mg/L
UV	1.62	0.67

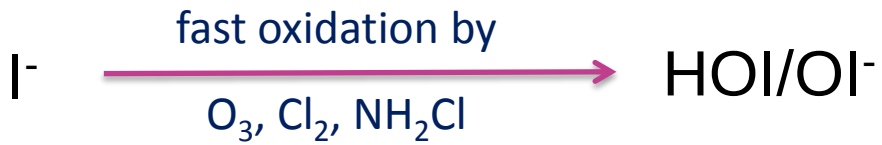
Speciation of I-halophenol after Chlorination/KI

- **Site B**
  - *2,4,6-triiodophenol:* ***55 %***
  - *2,4-dichloro-6-iodophenol:* ***45 %***
- **Site D**
  - *2,4-dichloro-6-iodophénol*

I-halophenols ~ 6 ng/L
Different products/Site

Implications for drinking water facilities

- Kinetics of iodide oxidation in the disinfection of natural waters



Disinfectant	I- oxidation time	HOI half-life
O3	< 1 ms	0.19 – 3.7 s
Cl2	< 1 ms	8 min – 10 h
NH2Cl	< 15 min	Long (> 1 y)

I_{org}:

- **O_3: Unlikely**
- **Cl_2: Limited probability compared to Cl-DBP**
- **NH_2Cl: very favorable**

Conclusions & Outlooks

Subtitle

Conclusions

- Multishot SBSE-GC/MS for the monitoring of I-halophenols
- LOD equal to 0.1 ppt reached successfully
- Only 9 standard available
- Possible qualitatif screening of all the congeners by SIM/Scan method
- Low occurrence in natural waters
- Safe drinking water facilities

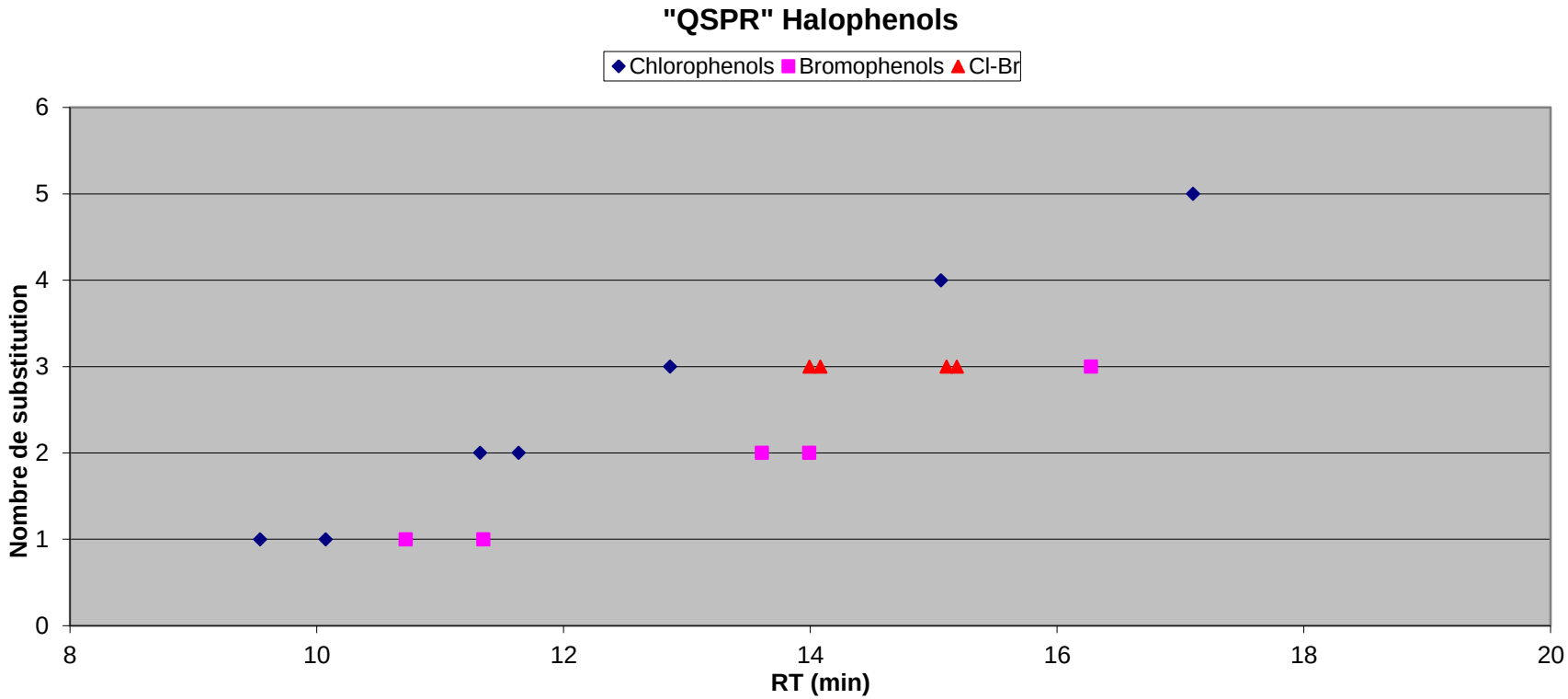
Evaluate the toxicity of the I-Halophenol class

Correlate the fate of I-halophenols to **I-THM**

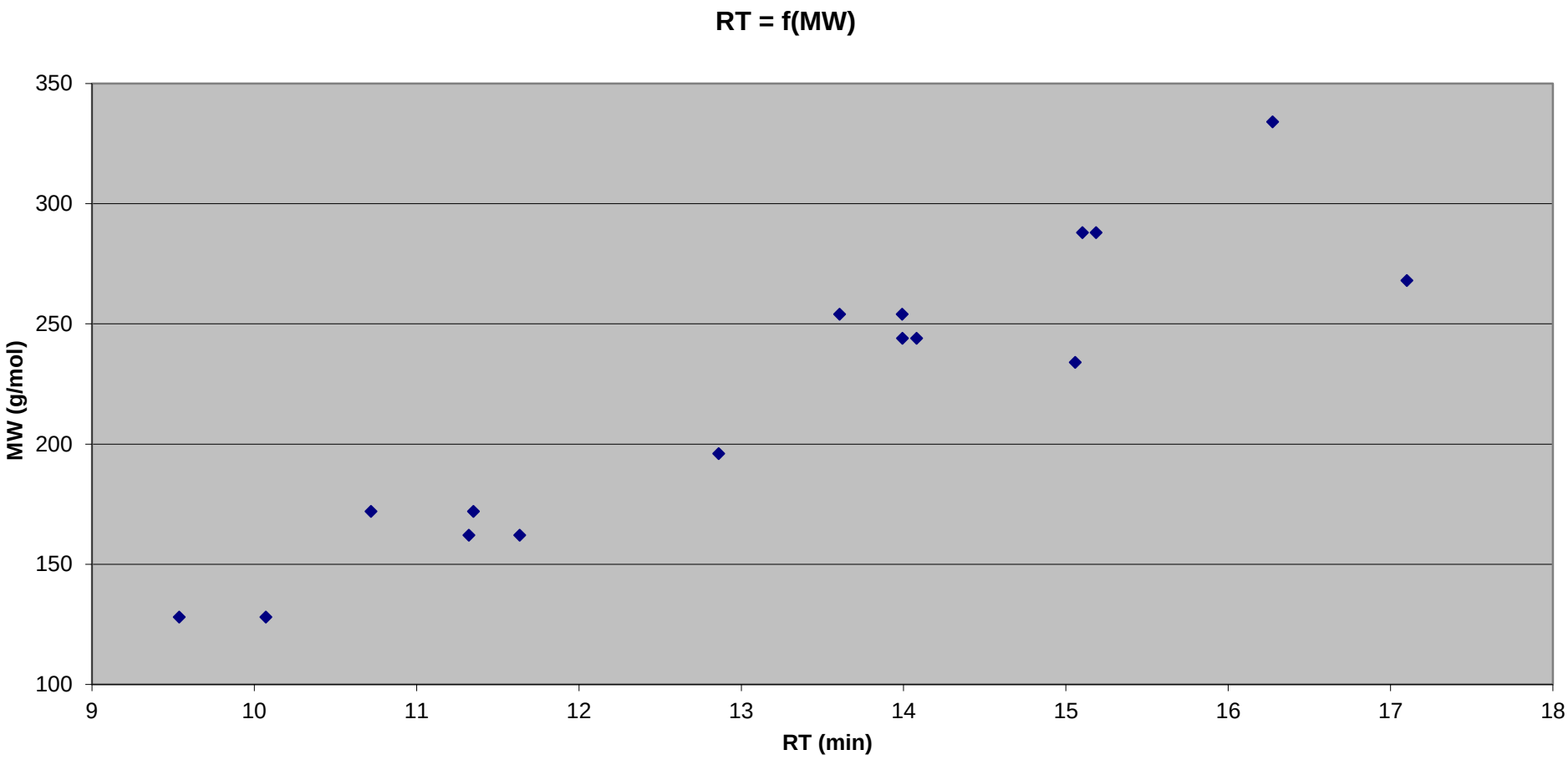
Target I-halophenols

Iodinated Halophenol	Molecular Formula Nominal MW (g/mol)	Cl-Br ratios	Log $K_{o/w}$
2-Iodophenol	C_6H_5OI (220)		2.68
4-Iodophenol			
6-Iodophenol			
2-Iodo, 4 -chlorophenol	C_6H_4OICl (254)	M: 100 M+2: 33	3.32
2-Iodo, 6 -chlorophenol			
2-Chloro, 4 - iodophenol			
2-Iodo, 4 -bromophenol	C_6H_4OIBr (298)	M: 100 M+2: 98	3.57
2-Iodo, 6 -bromophenol			
2-Bromo, 4 - iodophenol			
2,4 – Dichloro, 6 – iodophenol	$C_6H_3OICl_2$ (288)	M: 100 M+2: 65 M+4: 11	3.97
2,6 – Dichloro, 4 – iodophenol			
2,4 – Dibromo, 6 – iodophenol	$C_6H_3OIBr_2$ (376)	M: 51 M+2: 100 M+4: 49	4.46
2,6 – Dibromo, 4 – iodophenol			
2-Iodo,4-chloro,6-bromophenol	$C_6H_3OIClBr$ (332)	M: 77 M+2: 100 M+4: 24	4.21
2-Iodo,4 –bromo, 6-chlorophenol			
2-Chloro, 4-iodo, 6-bromophenol			
2,4-Diiodophenol	$C_6H_4OI_2$ (346)		3.86
2,6-Diiodophenol			
2,4-Diiodo, 6 - chlorophenol	$C_6H_3OI_2Cl$ (380)	M: 100 M+2: 33	4.49
2,6-Diiodo, 4 - chlorophenol			
2,4-Diiodo, 6 - bromophenol	$C_6H_3OI_2Br$ (424)	M: 100 M+2: 98	4.74
2,6-Diiodo, 4 - bromophenol			
2,4,6-Triiodophenol	$C_6H_3OI_3$ (472)		5.01

Correlation RT and nature of halogen



Correlation RT & MW



SIM method for I-halophenols

Composé	Temps d'élution (min)	Groupe SIM	Start time	Ions spécifiques (m/z)	Dwell
2-Iodophénol	14.197	1	10	220, 262	100
4-Iodophénol	14.898				
ICP et IBrP	Unknown	2	15.50	254, 256, 298, 300	50
2,4-Dichloro,6-iodophénol	17.451	3	17.30	288, 290, 292	100
IClBrP	Unknown	4	17.70	332, 334, 336 346 376, 378, 380 380, 382 424, 426	20
2,4,6-Triiodophénol	20.742	5	20.6	218, 472, 514	100