



ESR6

An experimental approach to examining correlation between external exposure and human body burdens

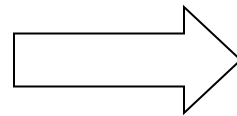
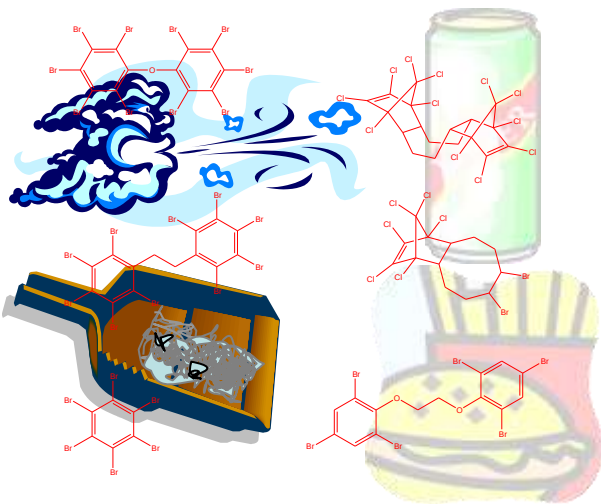
WP2 – Human Exposure
(Pathways and Monitoring)

Enrique Cequier

September 2011, Antwerp

INFLAME

Assessing pathways for human exposure to emerging flame retardants by comparing external doses from measurements in indoor **air** and **dust** as well as **food** and **beverages** and compare these with internal doses obtained through bio-monitoring



$\sum$ FR in air, dust, beverages and food

$\approx$

$\sum$ FR in blood, urine, saliva or hair ?



Assessing pathways for human exposure to emerging flame retardants by comparing external doses from measurements in indoor **air** and **dust** as well as **food** and **beverages** and compare these with internal doses obtained through bio-monitoring

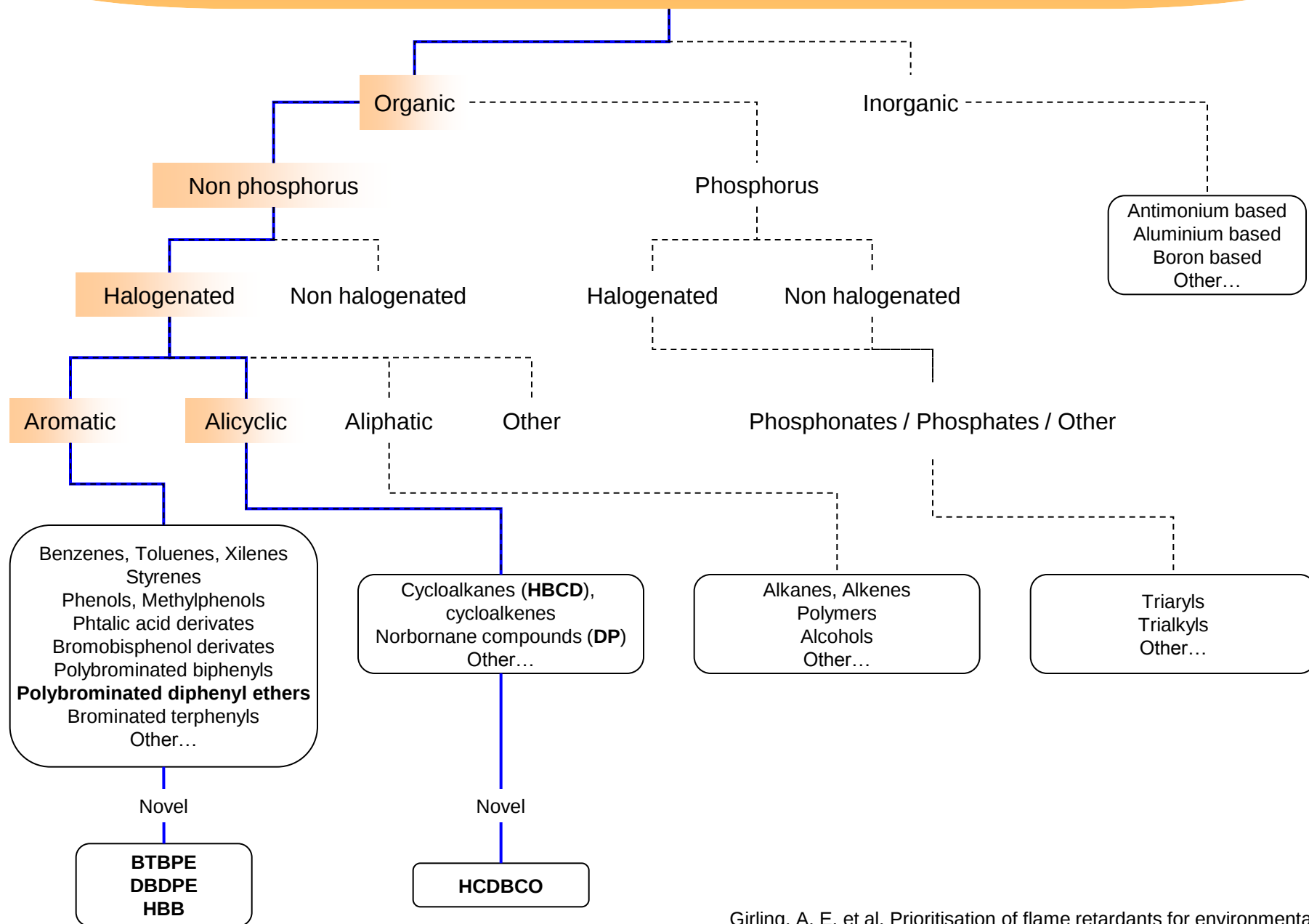
Develop selective and sensitive analytical methods for the determination of emerging:

- 1) persistent FRs in blood by means of GC/LRMS
- 2) metabolisable FRs in urine by means of LC/MS/MS

Background

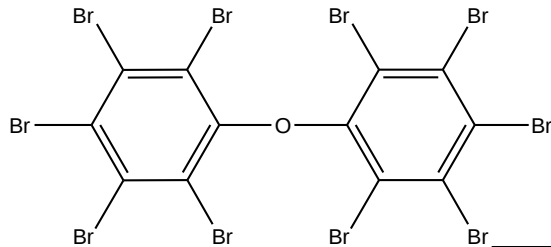
- ▶ Flame retardants are used to reduce or resist the spread of fire in a wide range of commercial and household products.
- ▶ Dechlorane plus, DBDPE, BDE209 and BTBPE are manufactured in a high production volumes (>1000 tons/year).
- ▶ Long-range atmospheric transport (they have been found in the Arctic).
- ▶ Persistent, toxic and can accumulate in biota and humans.
- ▶ Detected in air, dust, soil, sewage sludge, animal tissues and human blood (DP, HBB and BDE209).

Flame Retardants



Flame retardants structures

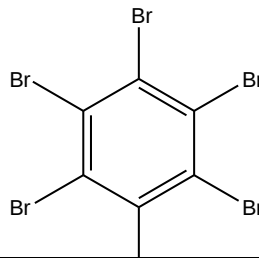
BDE209



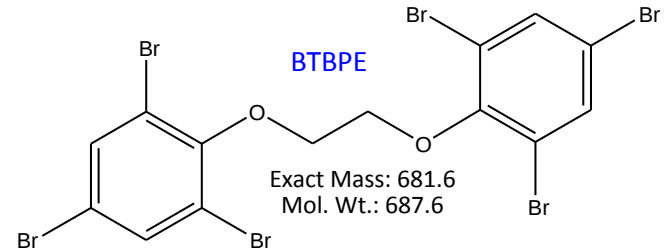
Exact Mass: 949.2
Mol. Wt.: 959.2

Decabromodiphenylether

HBB



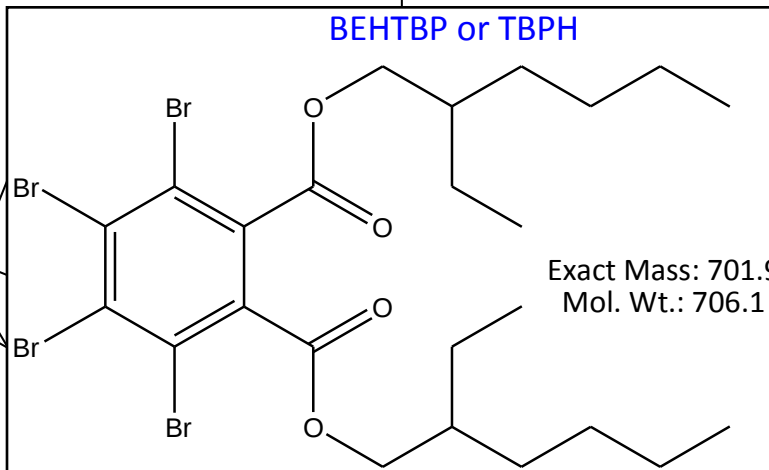
BTBPE



Exact Mass: 681.6
Mol. Wt.: 687.6

(2,4,6-tribromophenoxy)ethane

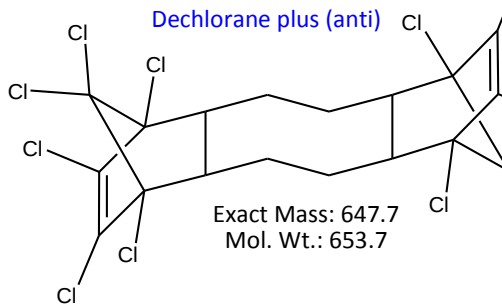
BEHTBP or TBPH



Exact Mass: 701.9
Mol. Wt.: 706.1

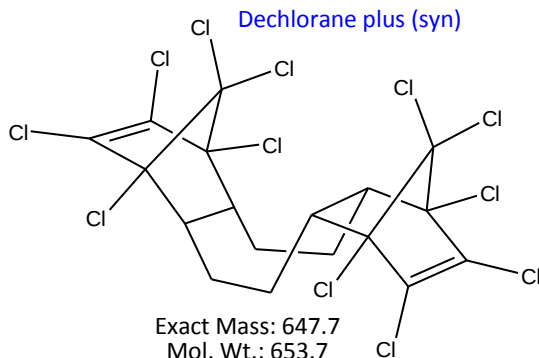
Bis(2-ethylhexyl)tetrabromophthalate

Dechlorane plus (anti)



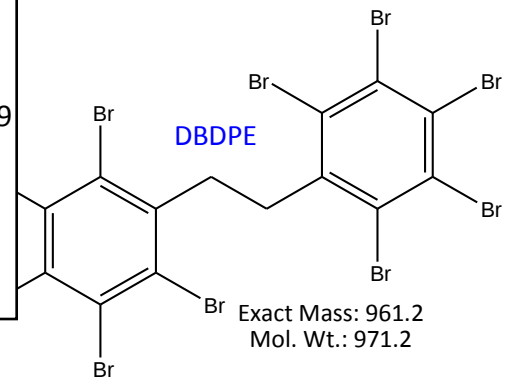
Exact Mass: 647.7
Mol. Wt.: 653.7

Dechlorane plus (syn)



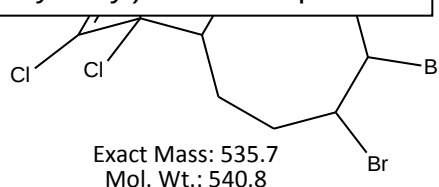
Exact Mass: 647.7
Mol. Wt.: 653.7

DBDPE



Exact Mass: 961.2
Mol. Wt.: 971.2

Decabromodiphenyl ethane



Exact Mass: 535.7
Mol. Wt.: 540.8

Hexachlorocyclopentadienyldibromocyclooctane

Dodecachlorododecahydrodimethanodibenzocyclooctene

Chromatography

GC/LRMS Method

Agilent 6890 (GC) 5973 (MS, single quadrupole)

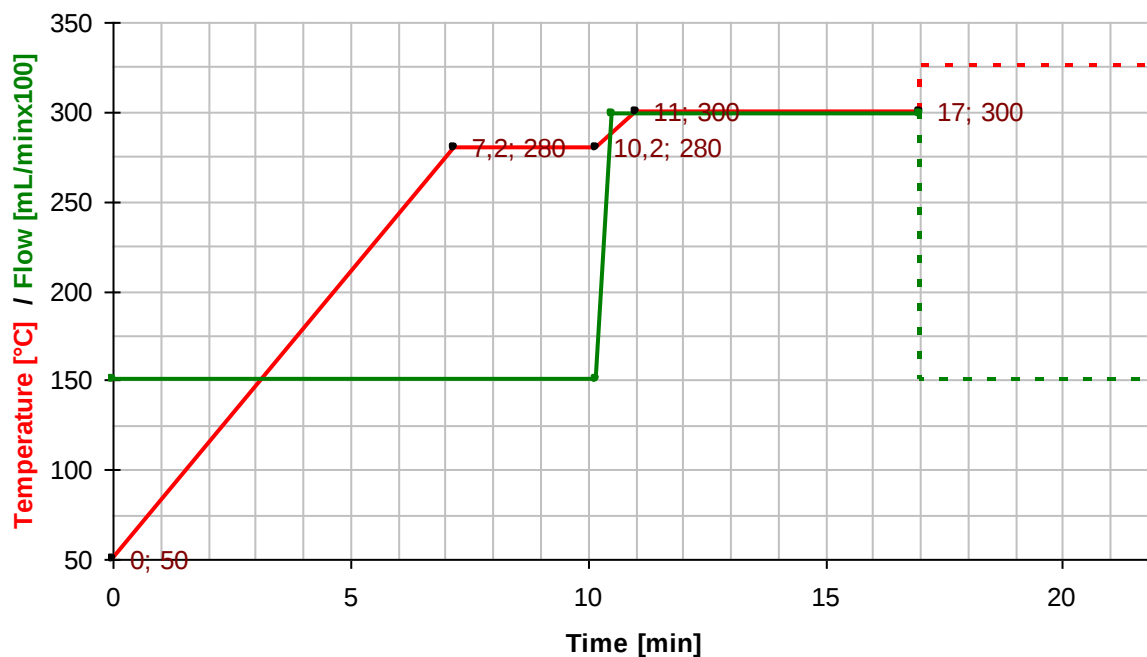
Column **DB5-MS** (15mx0,25mmx0,1µm)

Injection volume 1µL

Injection temperature 280 ° C

Pulsed splitless 55psi@2min

Temperature and flow program



Auxiliary temperature 280° C

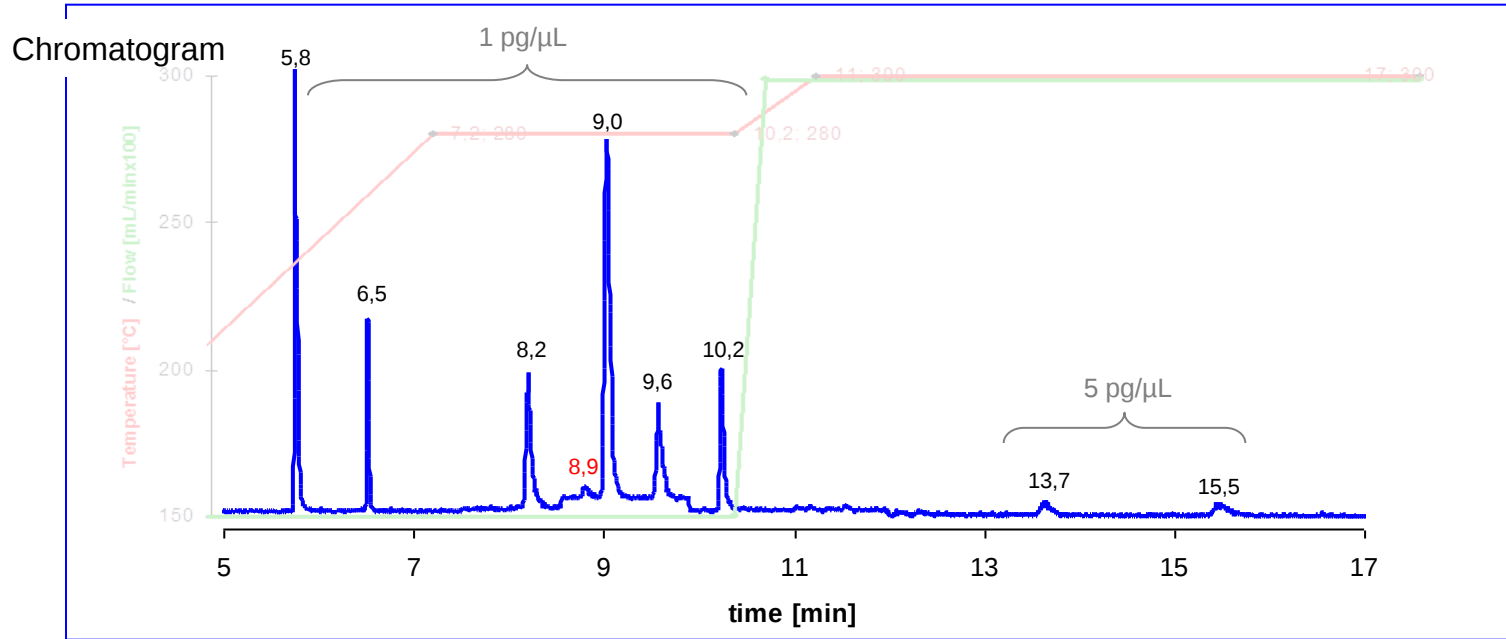
MS source 200° C

Reagent gas: CH₄ (40%;1,8x10⁻⁴Torr)

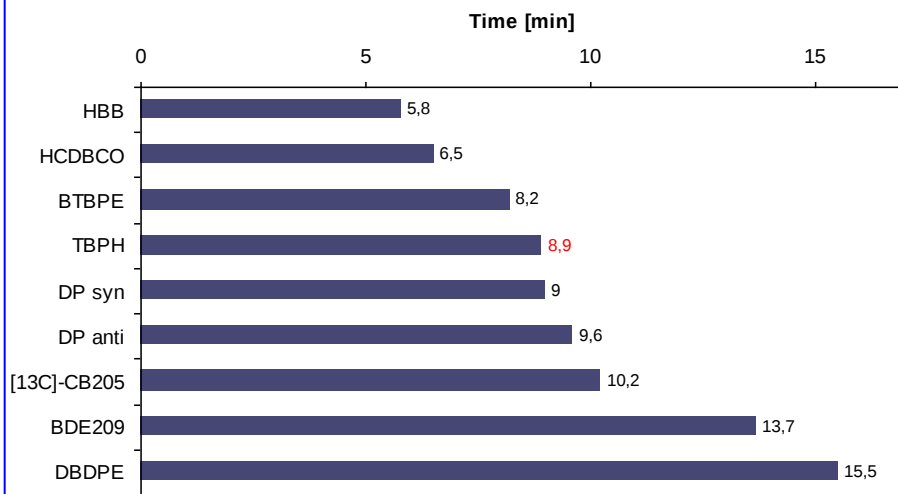
Ionization **ECNI** Detection **SIM**

	Window time [min]		Ions [m/z]	Dwell time [ms]
	Start	End		
HBB	5	6,2	79 / 471	50
HCDBCO	6,2	7,5	79 / 538	50
BTBPE	7,5	9	79 / 81	100
DPsyn and DP anti	9	10	652 / 654	50
[¹³ C]-CB205	10	12	573 / 651	100
BDE209 and DBDPE	12	17	79 / 81	100
DBDPE	12	17	79 / 81	100

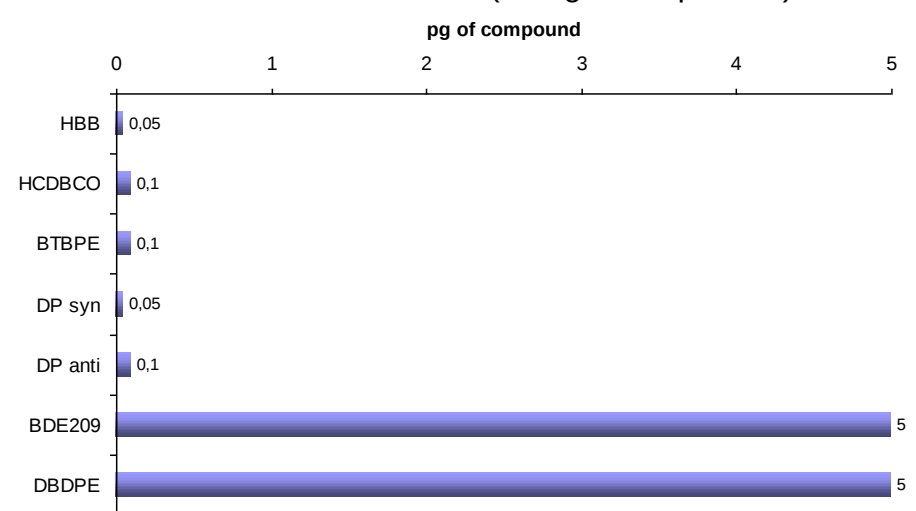
Chromatography



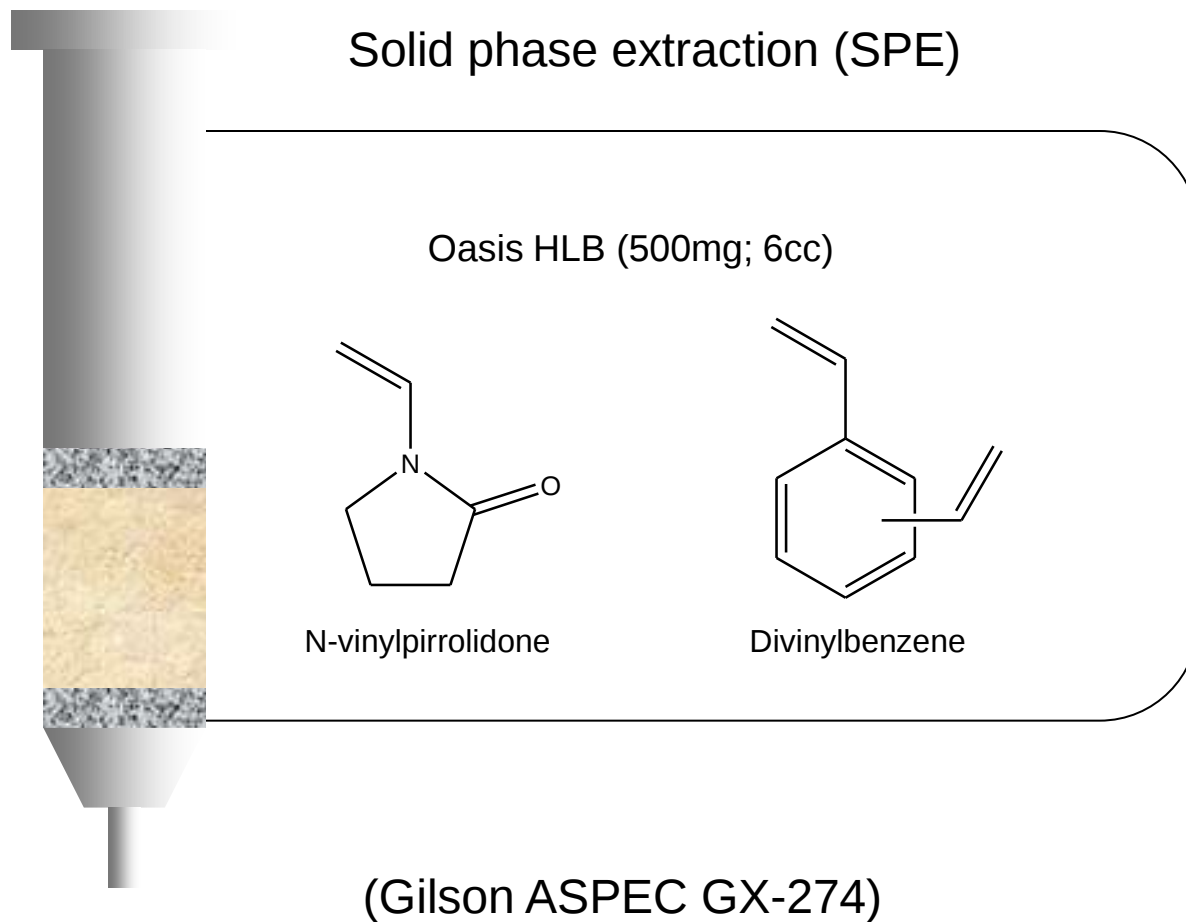
Retention times



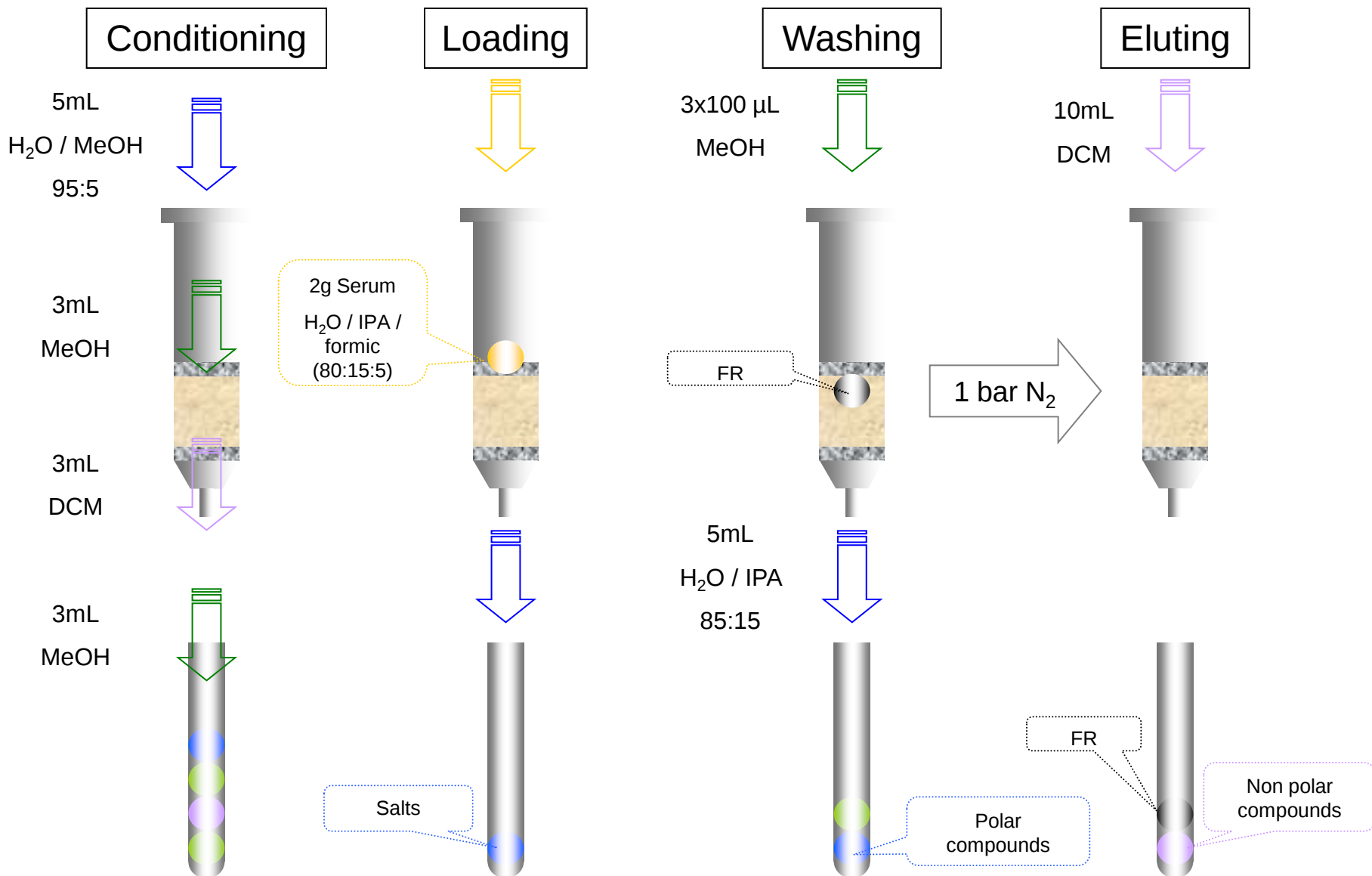
Instrument detection limits (7 target compounds)



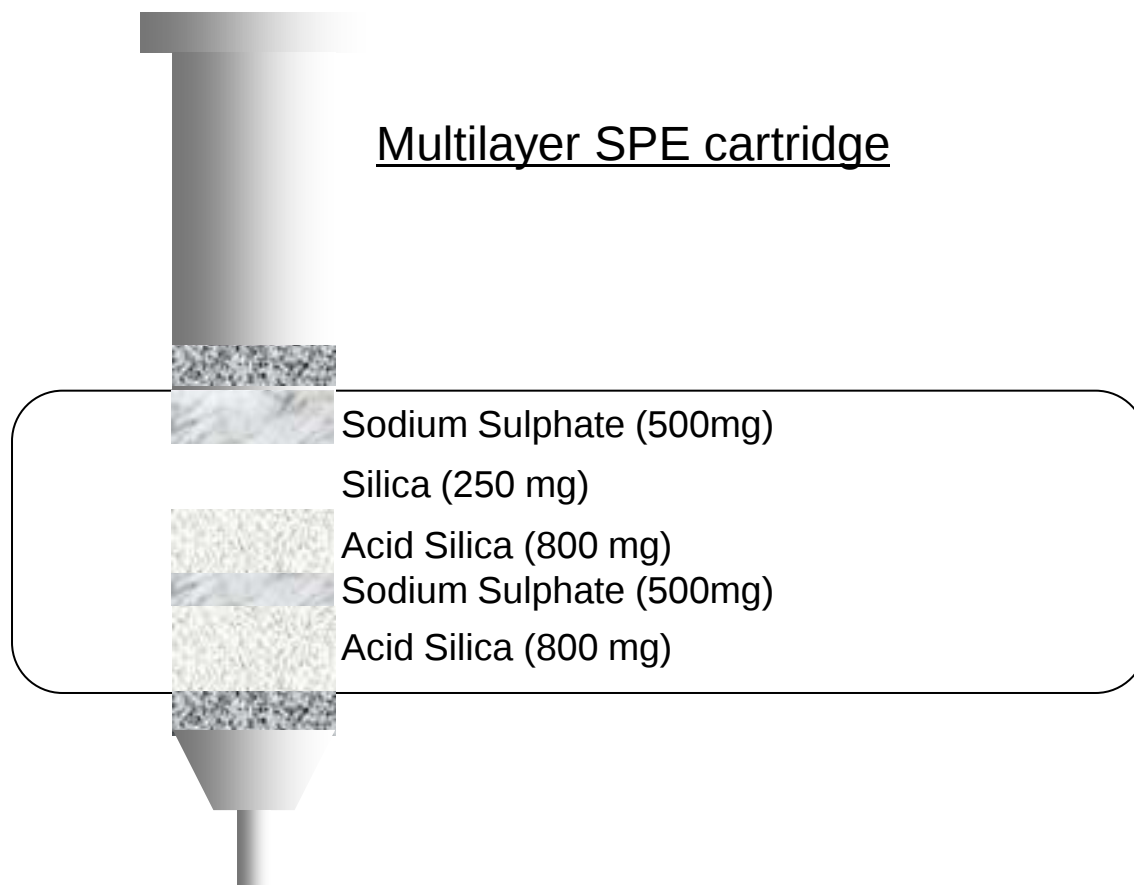
Extraction of analytes



Solid Phase Extraction



Clean up



Clean up "pass through"

Conditioning

5mL
Heptane / DCM
4:1



5mL
Heptane



Loading/collecting

10mL
Heptane / DCM
4:1



Lipids

5mL (SPE extract)
Heptane / DCM
4:1



FR

Recoveries

Spiking level 50 pg, except BDE209 and DBDPE 500 pg (n=6)

	HBB	HCDBCO	BTBPE	DP syn	DP anti	BDE209	DBDPE
%	94	80	106	37	75	86	32

Spiking level 1000 pg, except BDE209 and DBDPE 10000 pg (n=3)

	HBB	HCDBCO	BTBPE	DP syn	DP anti	BDE209	DBDPE
%	97	119	93	70	90	61	40

- ▶ Overall recoveries range from 32 to 119% !!!.
- ▶ Overall coefficients of variation range from 13 to 51% !!!.
- ▶ No internal standards used for these calculations, only recovery standard [^{13}C]-BDE205 before injection.
- ▶ **Preliminary results**, method must be optimized.

Future work

- ▶ SPE and clean up method optimization.
- ▶ Validation of the sample preparation and chromatographic method for the persistent FR.
- ▶ Sampling of indoor air and dust, urine, blood, saliva and hair from a selected cohort.
- ▶ GC/MS analyses of FR in real samples (serum) using internal standards.
- ▶ Method development and determination of metabolizable FR in urine by HPLC/MS/MS (QqQ).