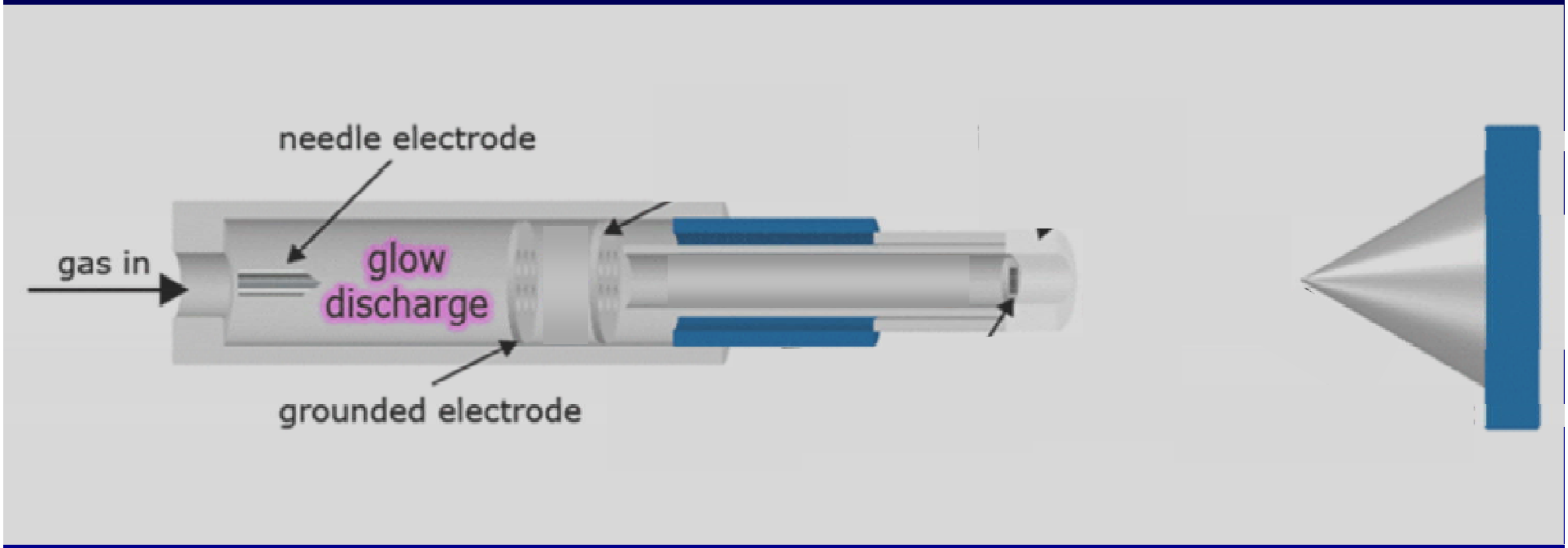
Assessing DART-MS for the Rapid Screening of Phthalates in Food Contact Polymers

Luke K Ackerman, Analytical Chemist, USFDA Center for Food Safety & Applied Nutrition

How does DART work?



$$He + e\text{-}^* \rightarrow He^*$$

$$He^* + H_20 \rightarrow H_20\cdot^+ + He + e\text{-}$$

$$H_20\cdot^+ + H_20 \rightarrow H_30^+ + OH\cdot$$

$$H_30^+ + M \rightarrow M{+}H^+ + H_20$$

JEOL Inst. Co. www.jeolusa.com

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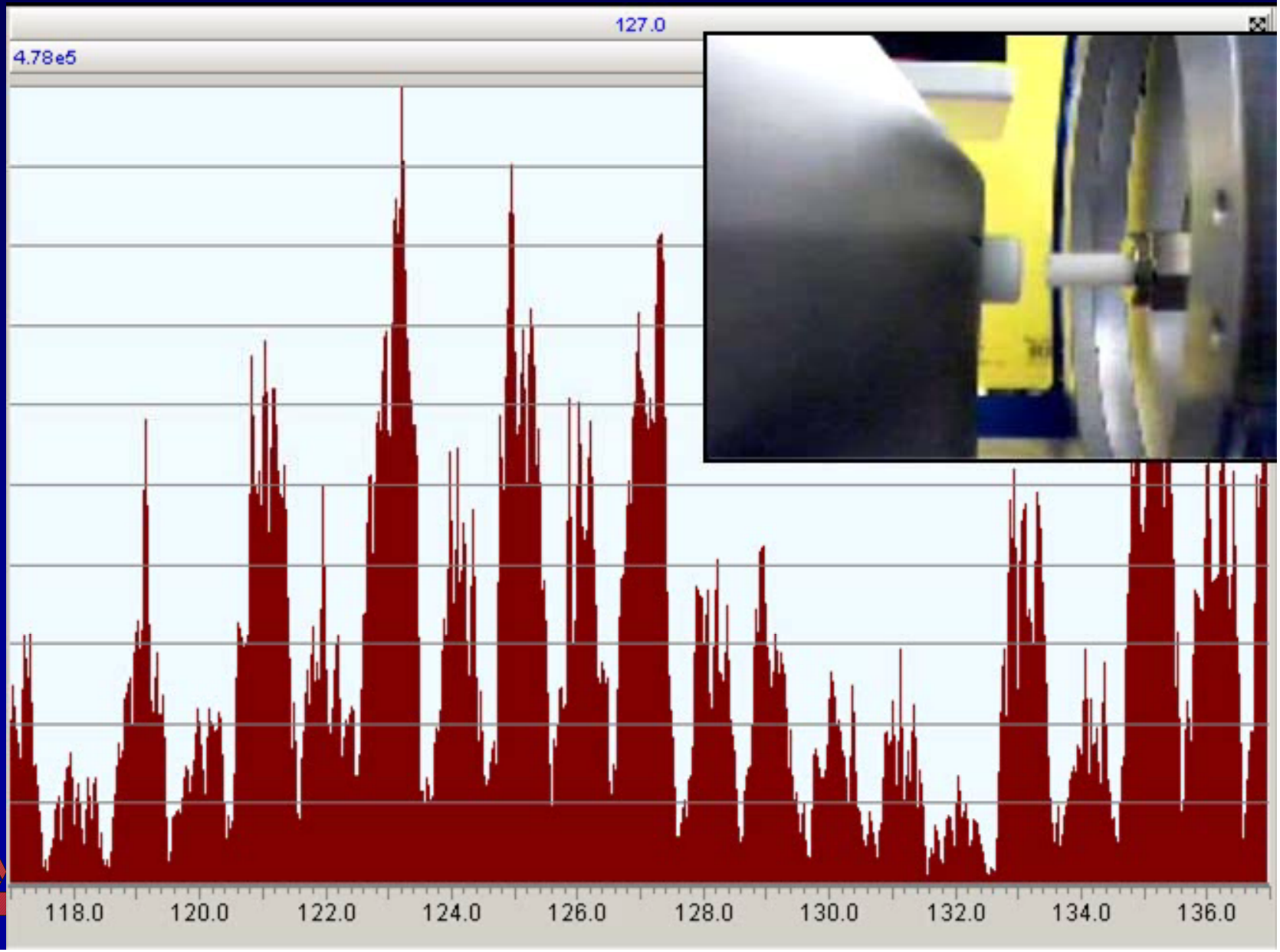

What does DART-MS measure?

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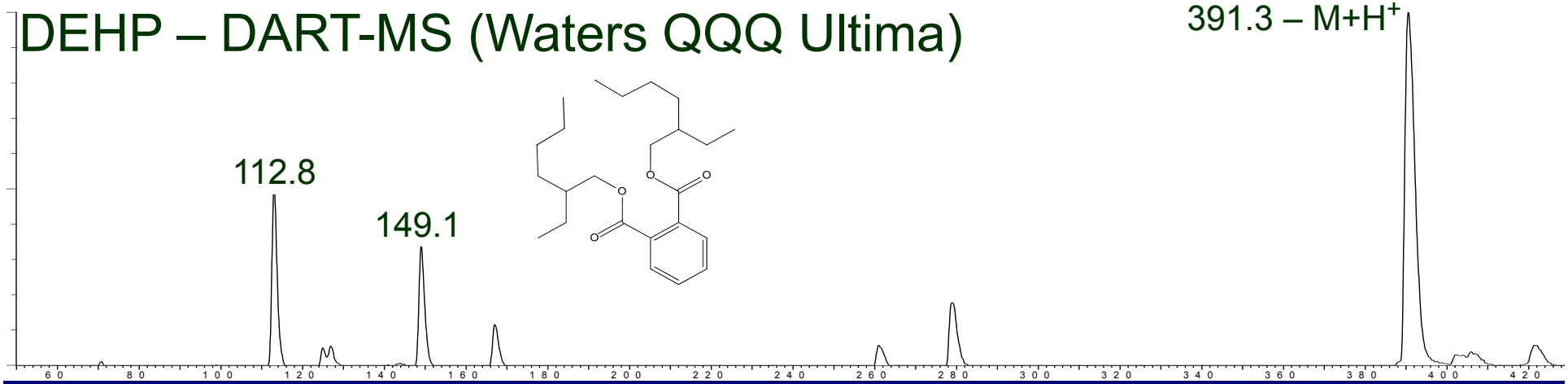
DEHP – DART-MS (Waters QQQ Ultima)



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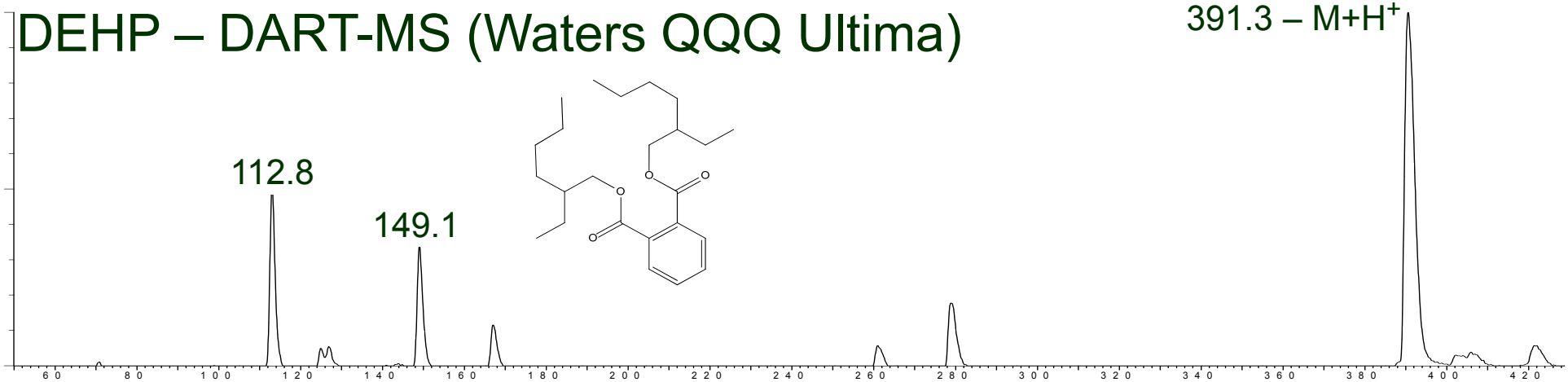

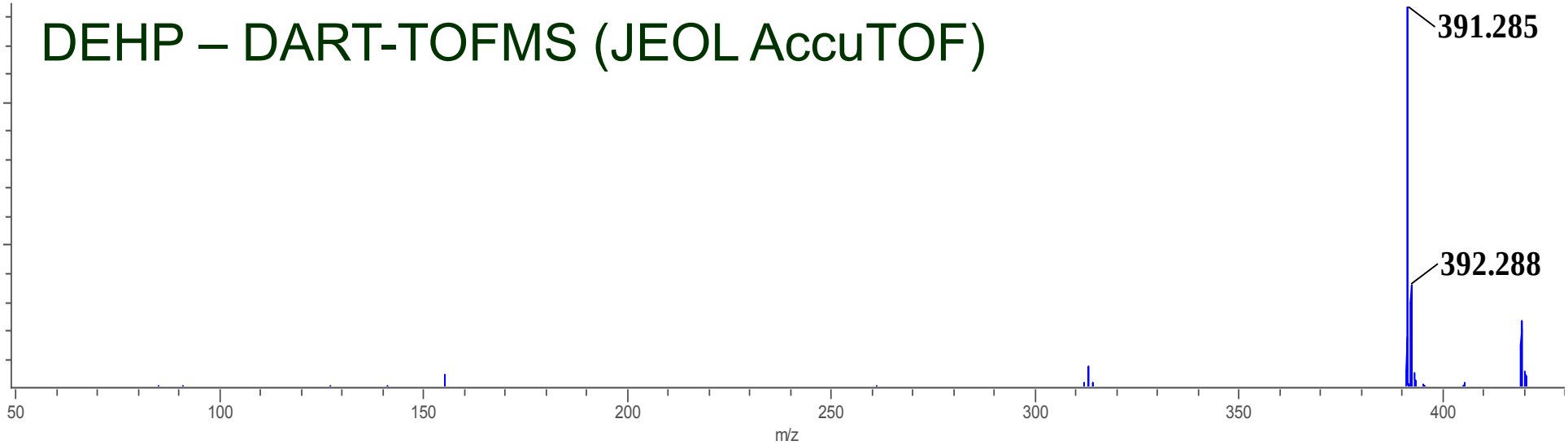

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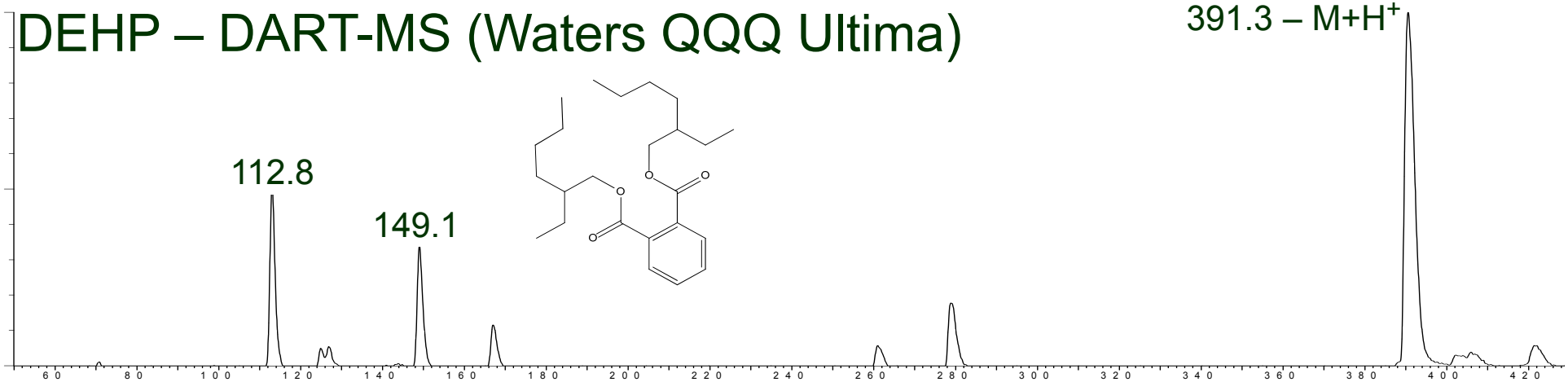
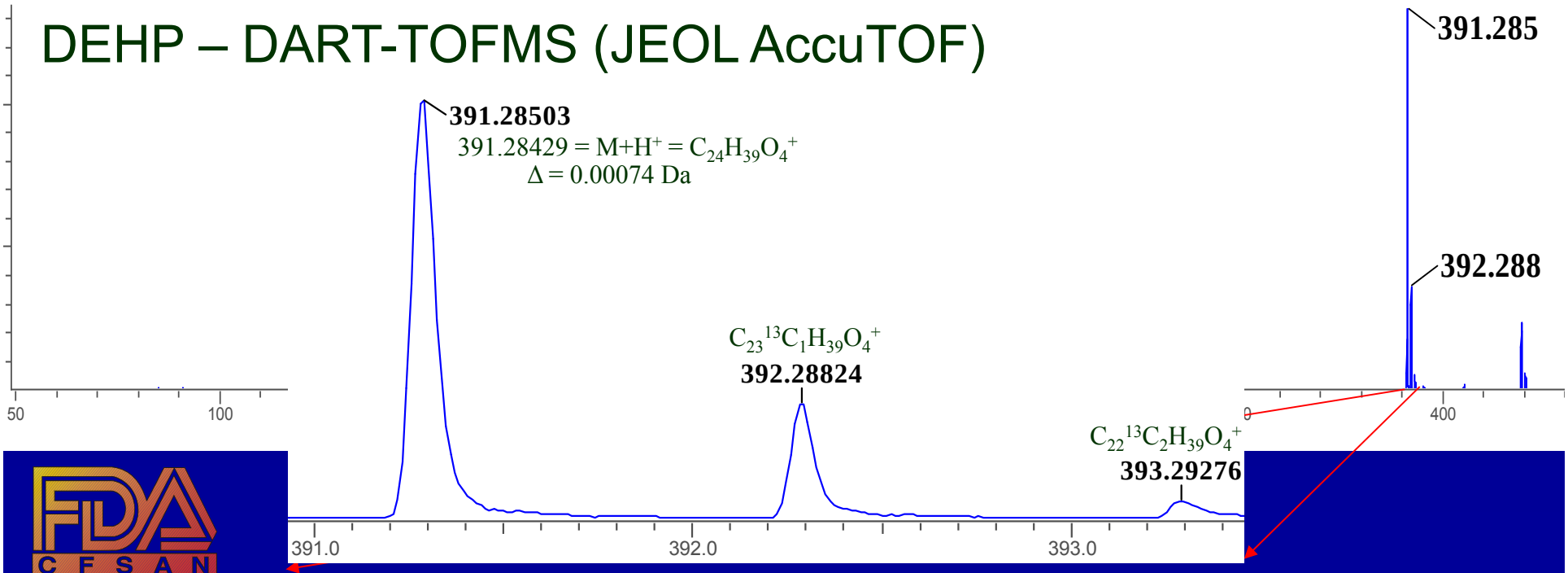


DEHP – DART-TOFMS (JEOL AccuTOF)



What is DART-MS Response?

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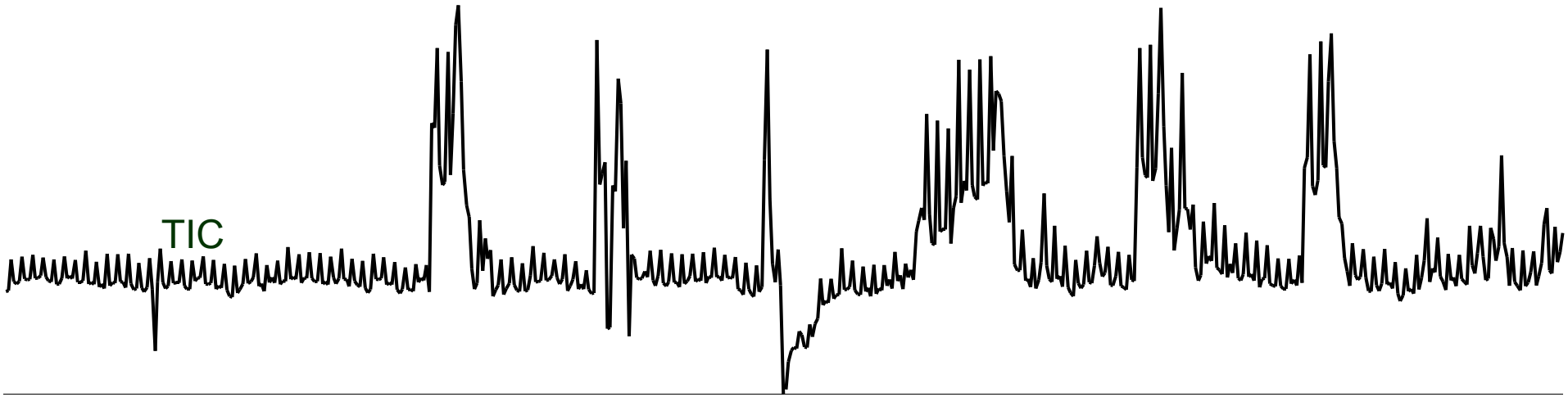

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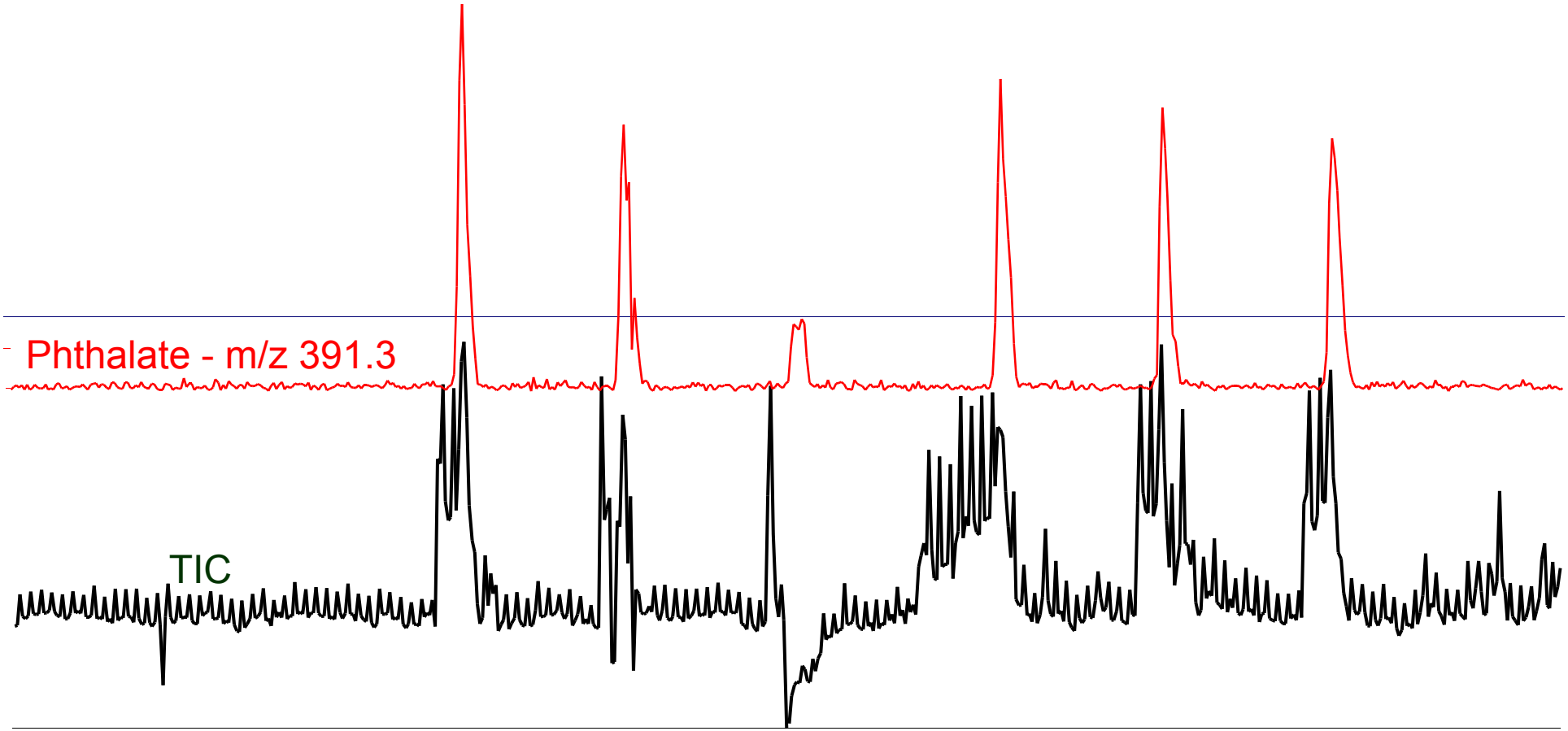

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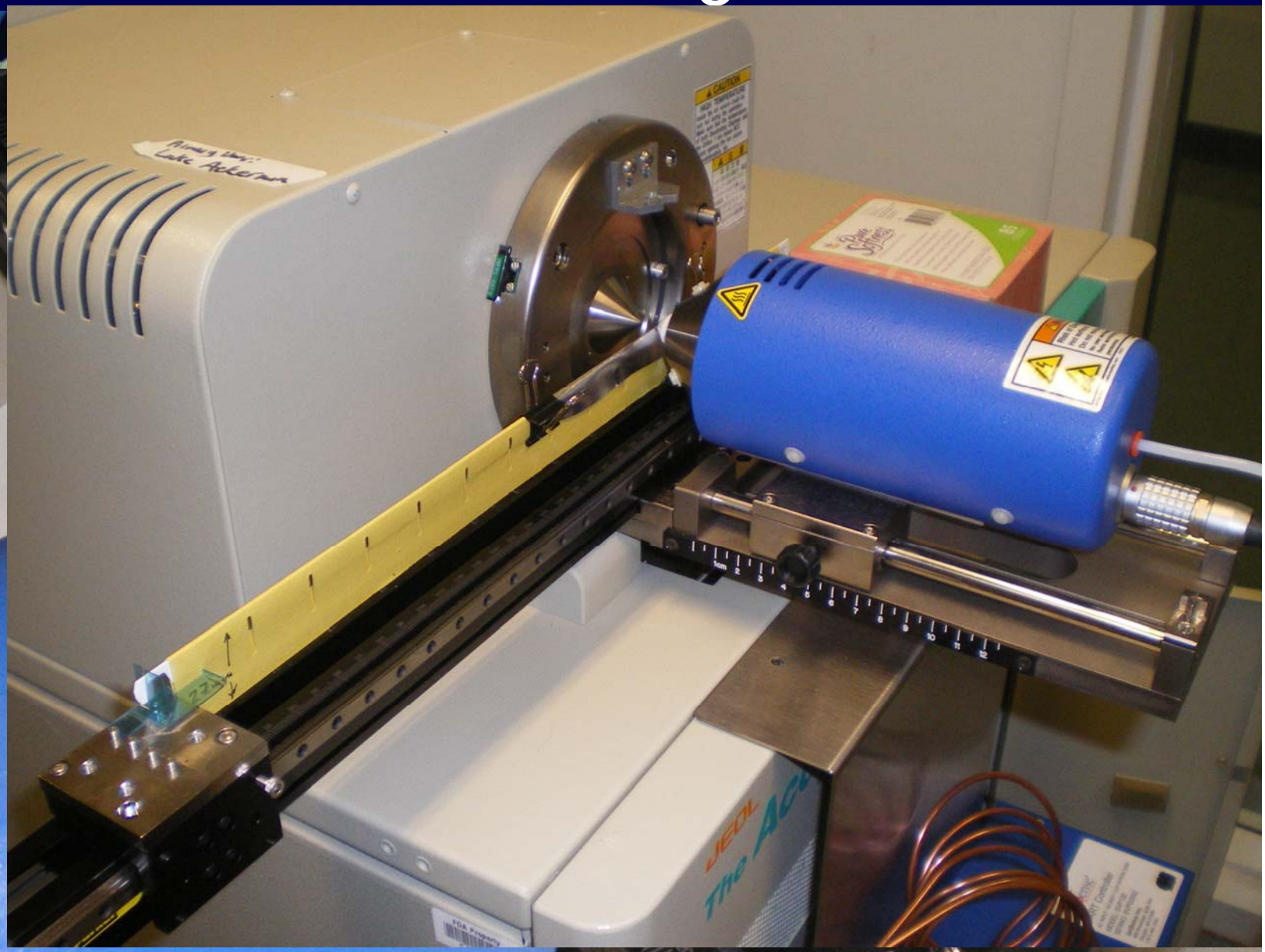
Different DART configurations.



Can DART-MS Quantitate?

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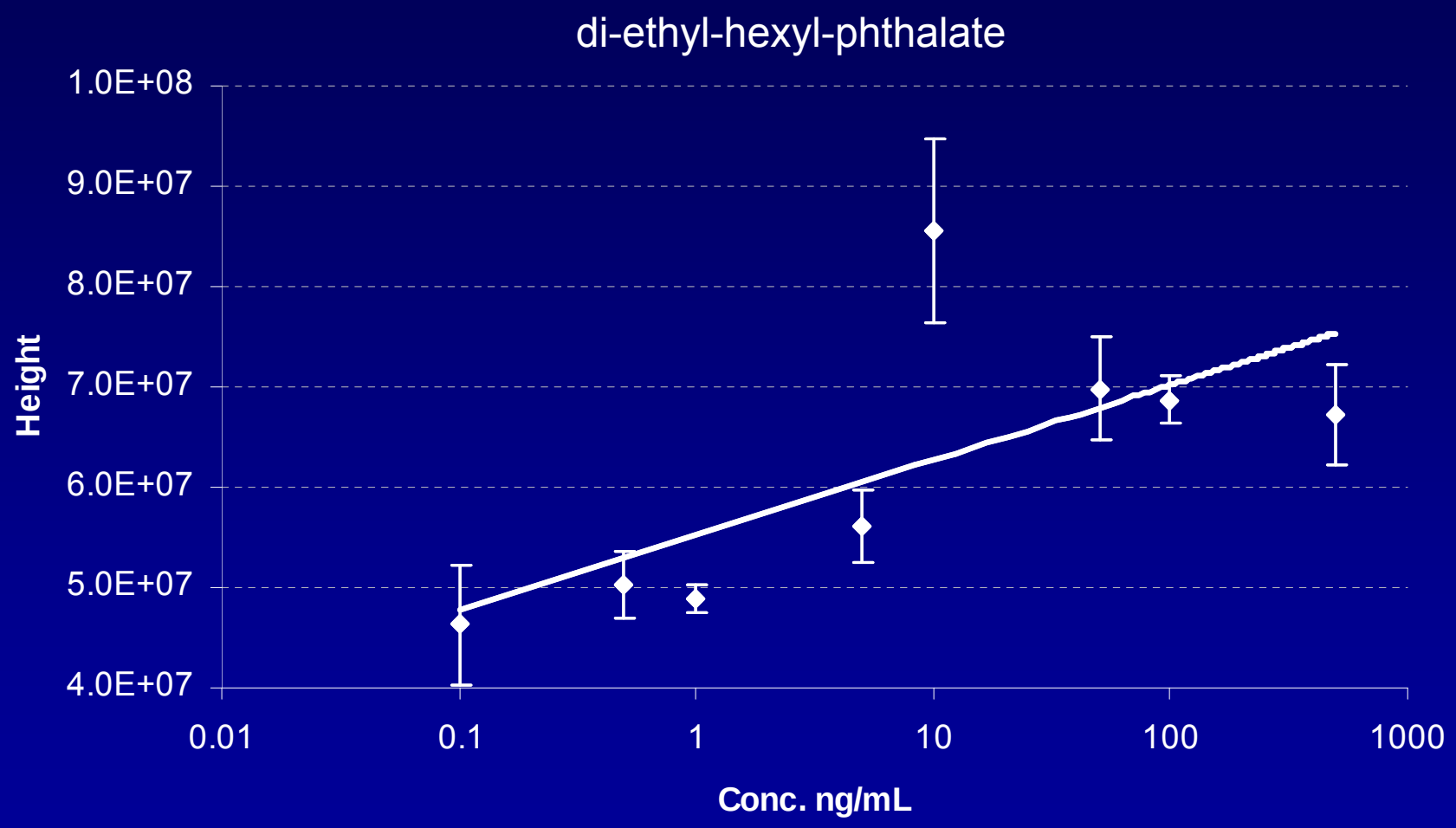
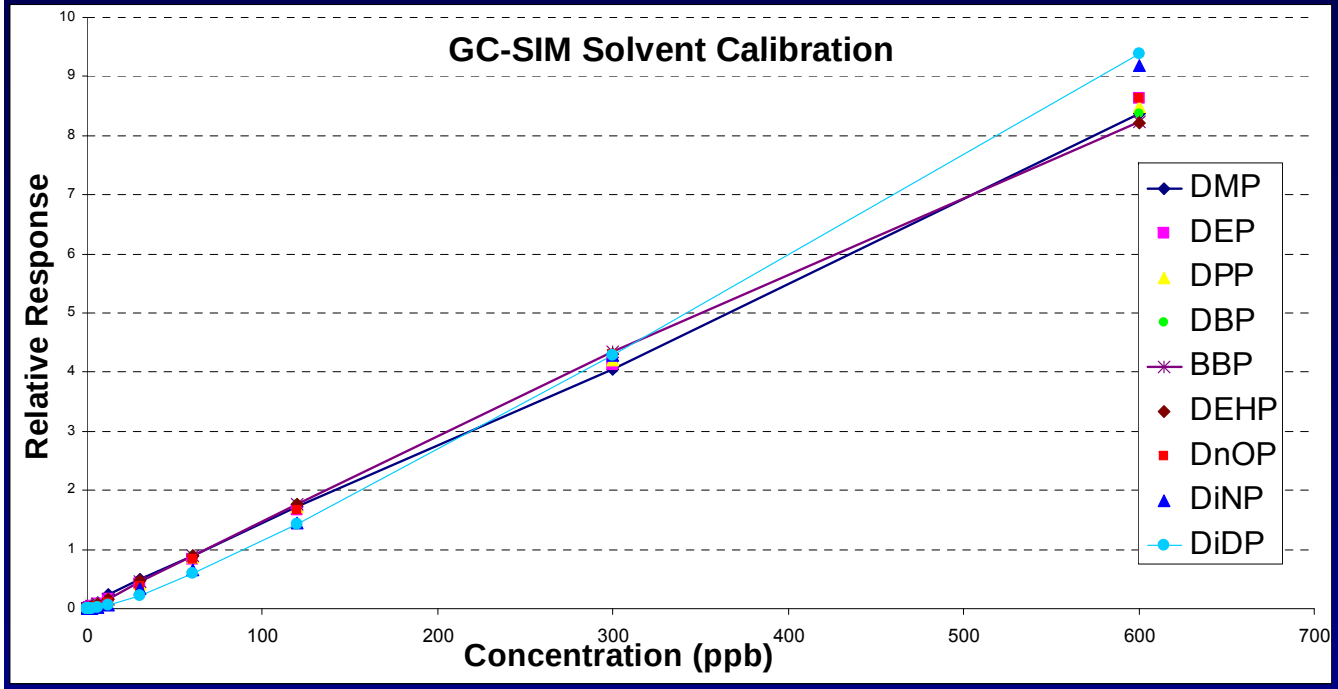
Can DART-MS Quantitate?



Phthalate Quantitation



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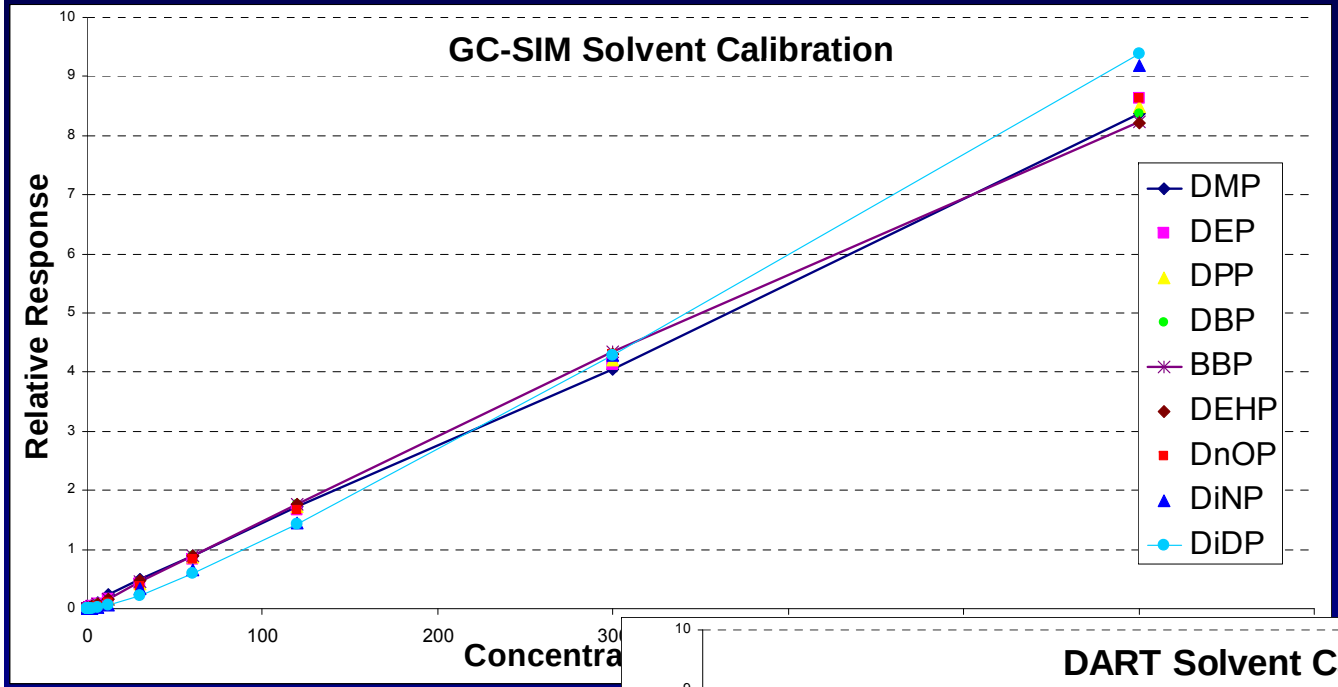

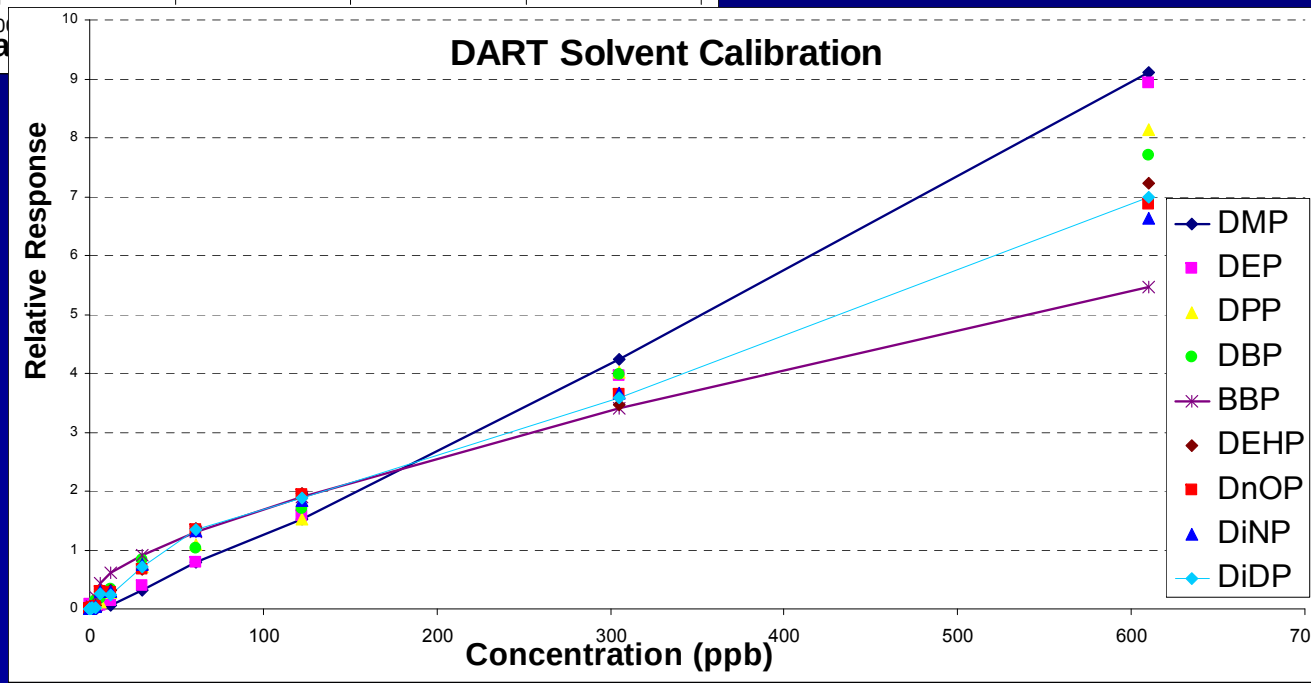

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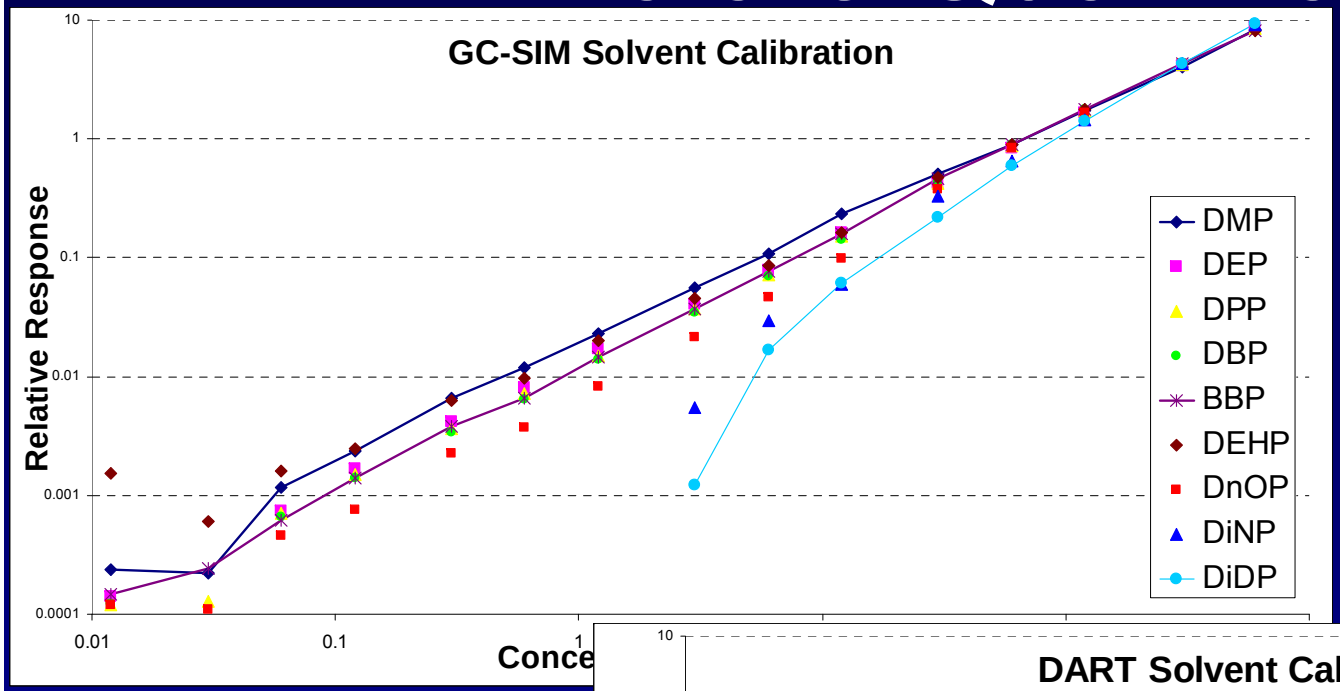

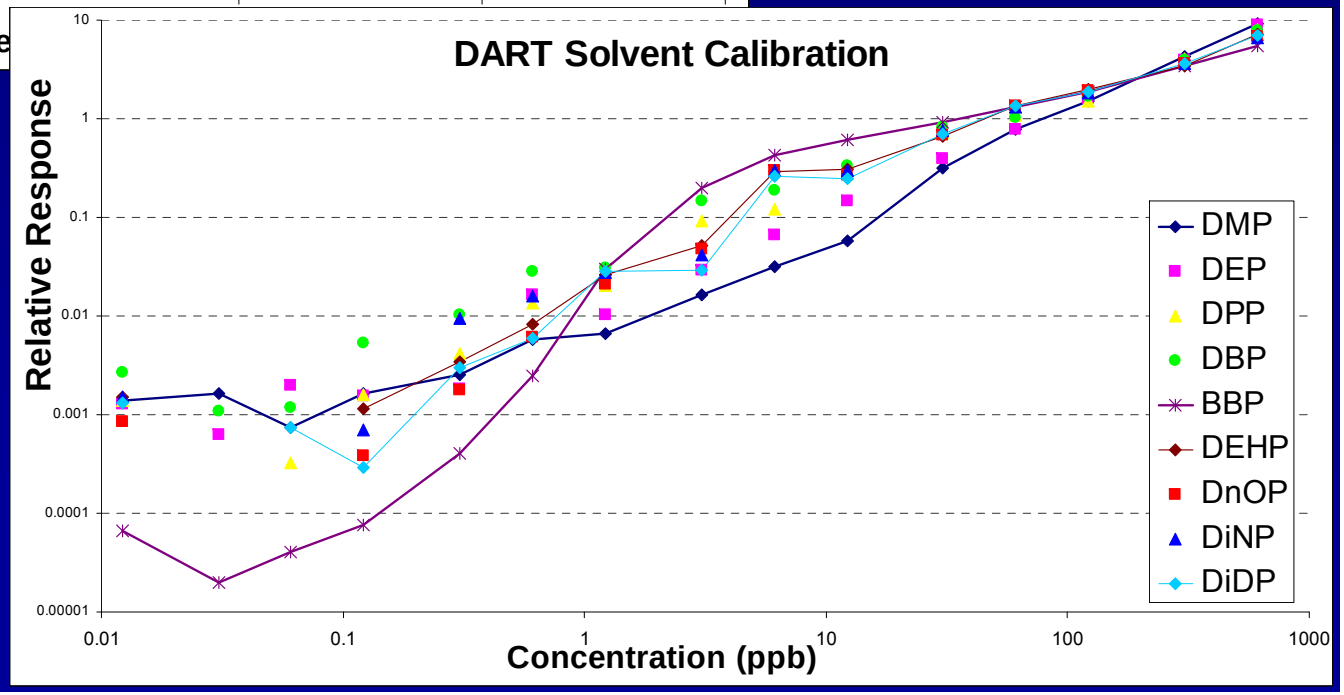

DART Sensitivity…on Polymers

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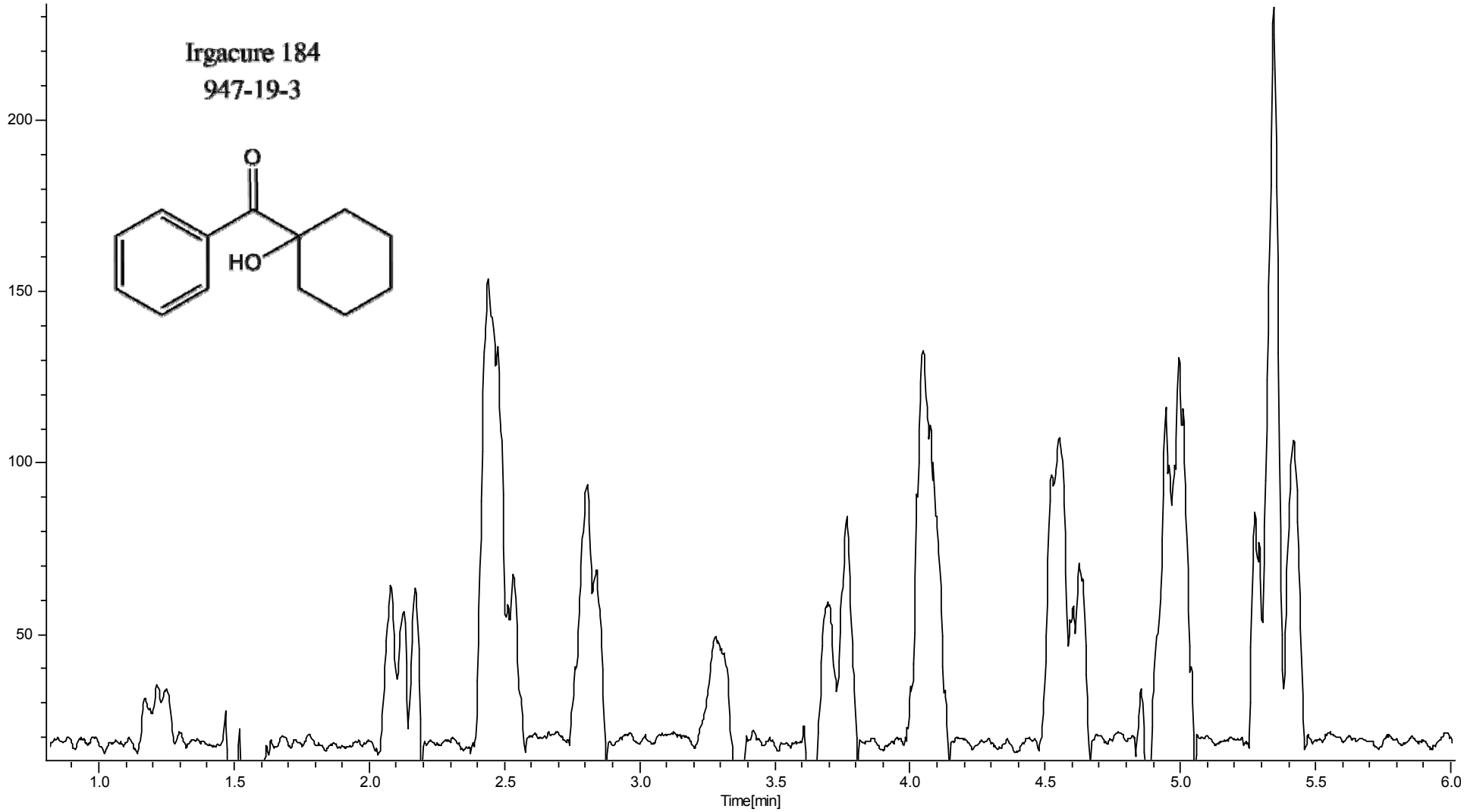

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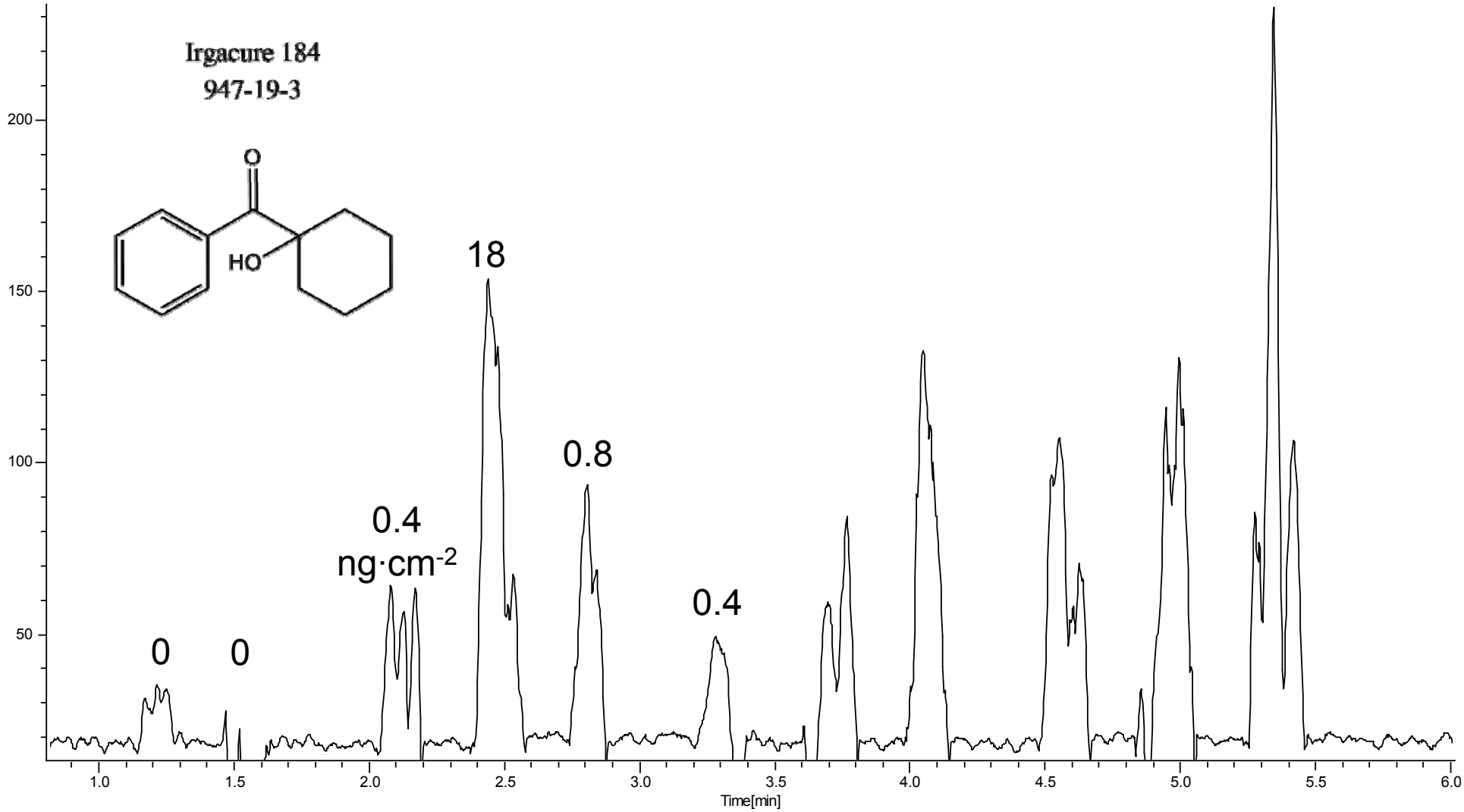

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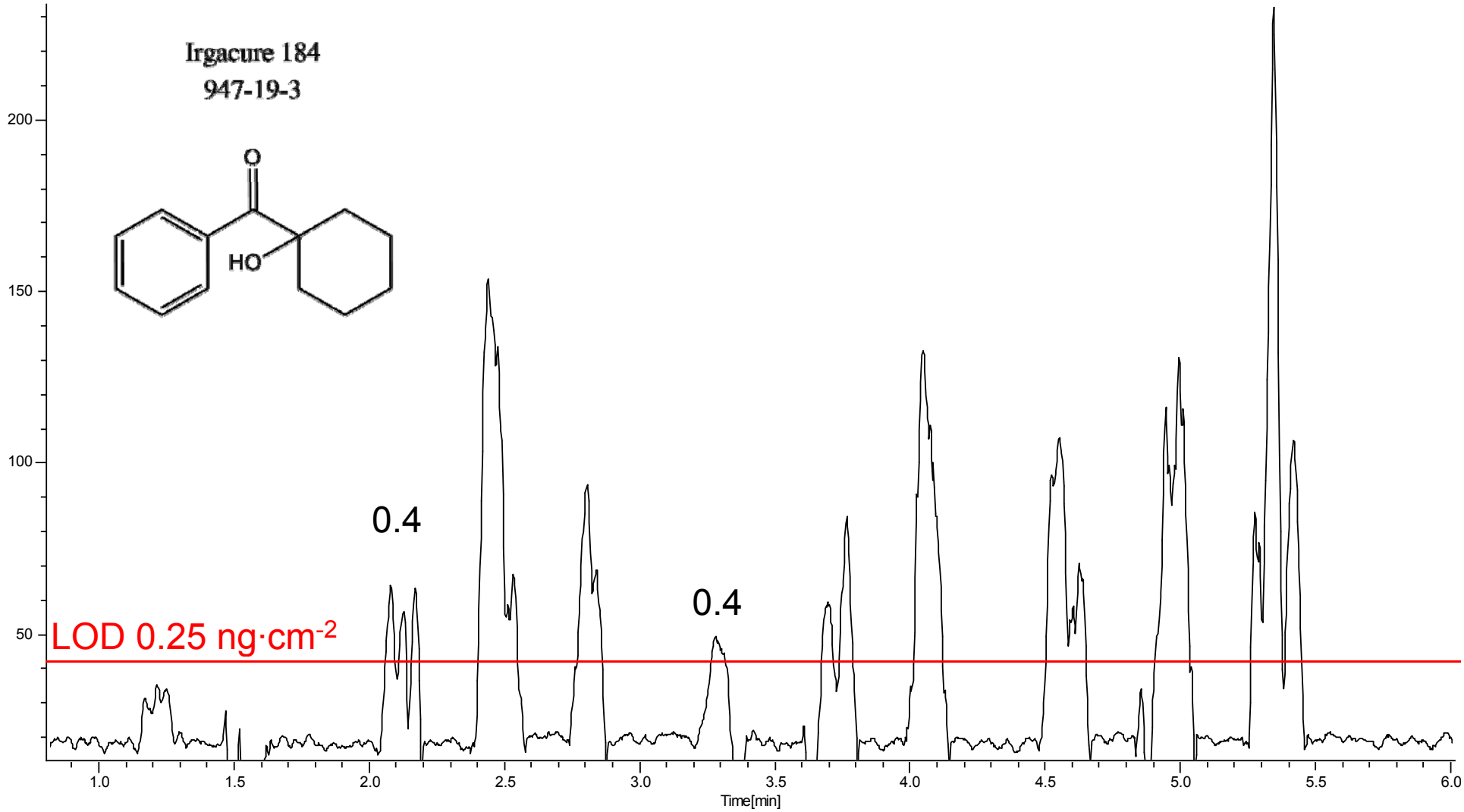

Can DART-MS Identify Phthalates?

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Can DART-MS Identify Phthalates?

Analyte	$M+H^+$	M-ethylene	M-ethenol
DMP	195.065	181.050	163.039
DEP	223.096	195.065	177.055
DPP	251.128	209.081	191.070
DBP	279.159	223.096	205.086
BBP	313.143	257.081	239.070
DEHP	391.284	279.159	261.149
DNOP	391.284	279.159	261.149
DINP	419.316	293.175	275.164
DIDP	447.347	307.190	289.180

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DART-MS Identification of Phthalates

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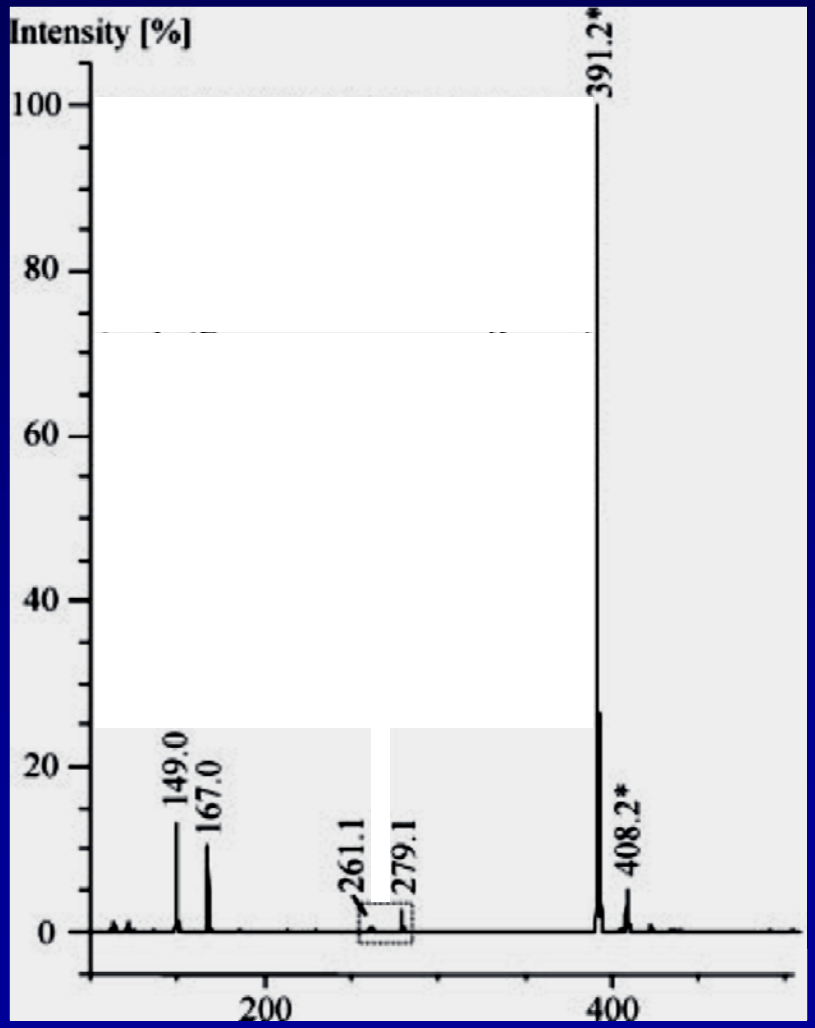
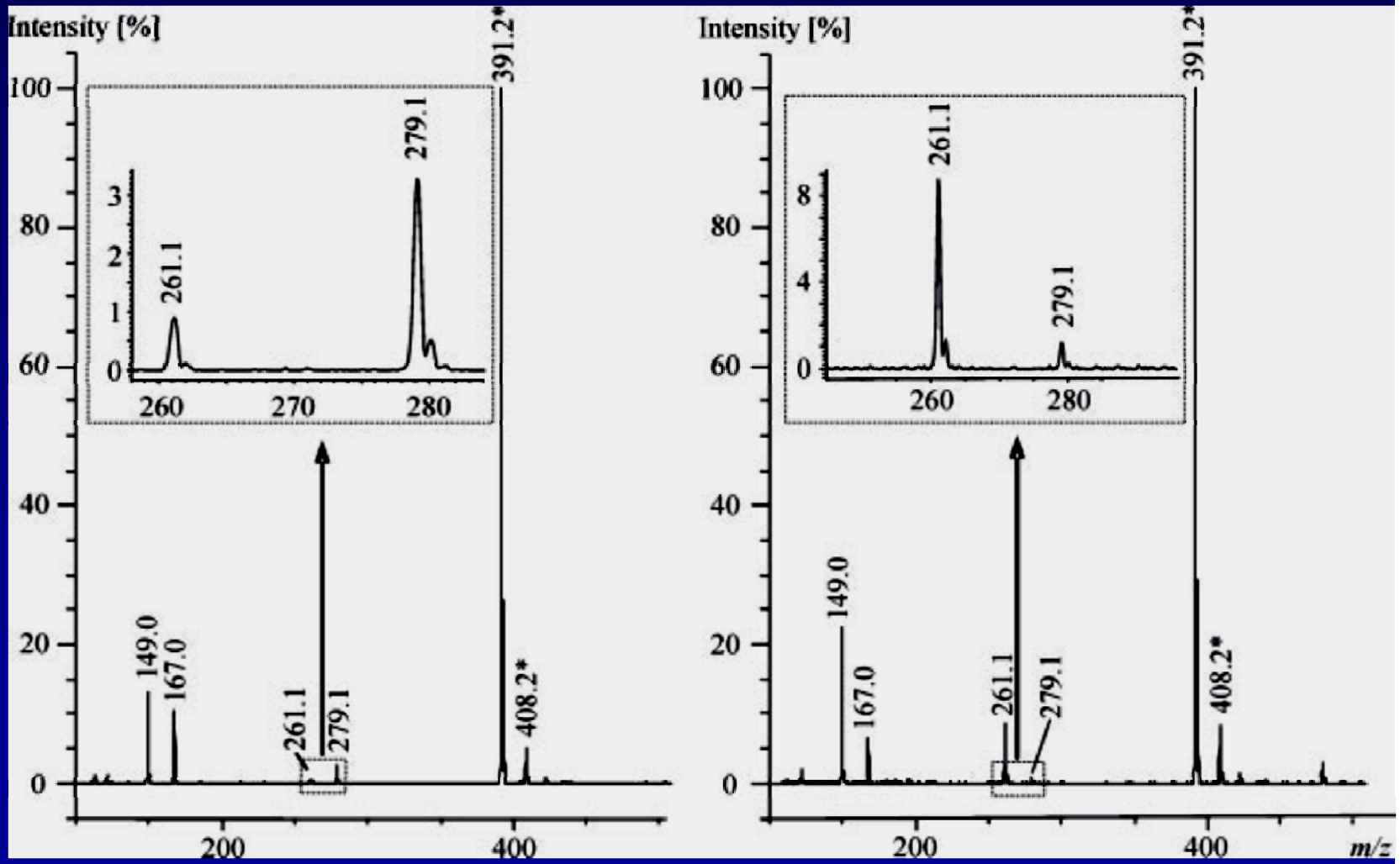


Adapted from Rothenbacher, Rapid Com. Mass Spec.,2009, 23(18)

DART-MS Identification of Phthalates

DEHP

DnOP



DEHP m/z 279 = 3.3 x 261
DnOP m/z 279 = 0.11x 261

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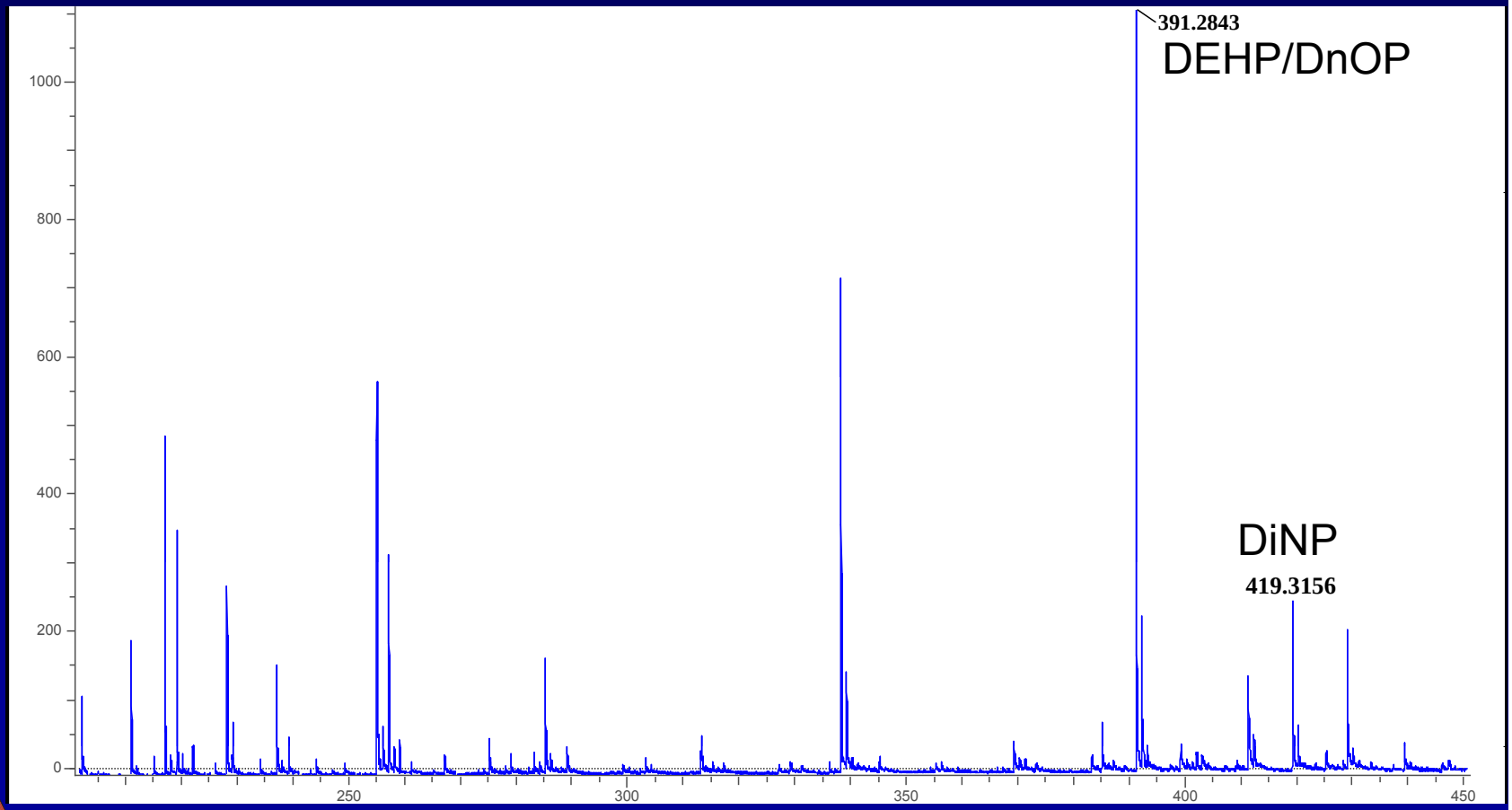
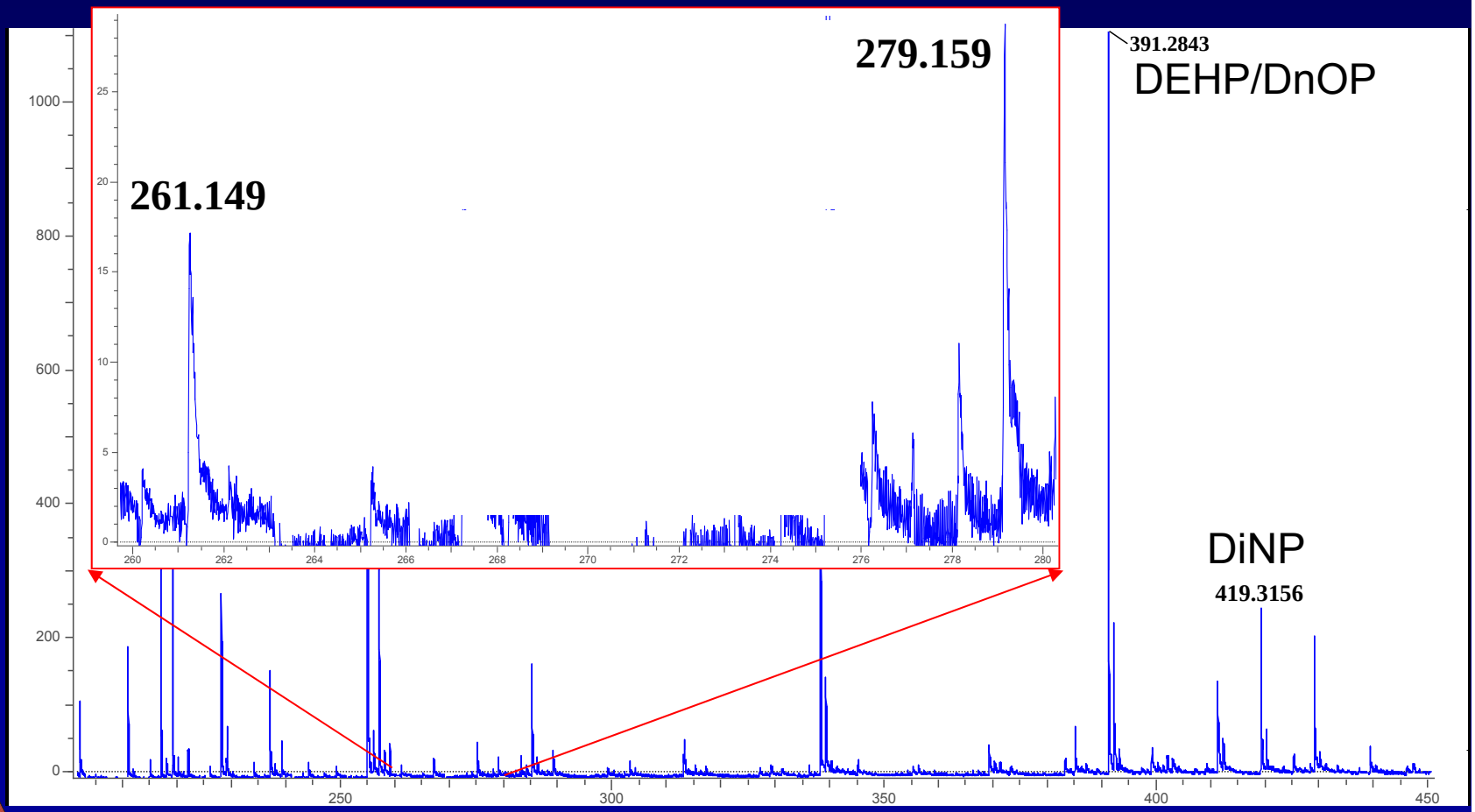
DART id of phthalates in PP/LDPE



DART id of phthalates in PP/LDPE



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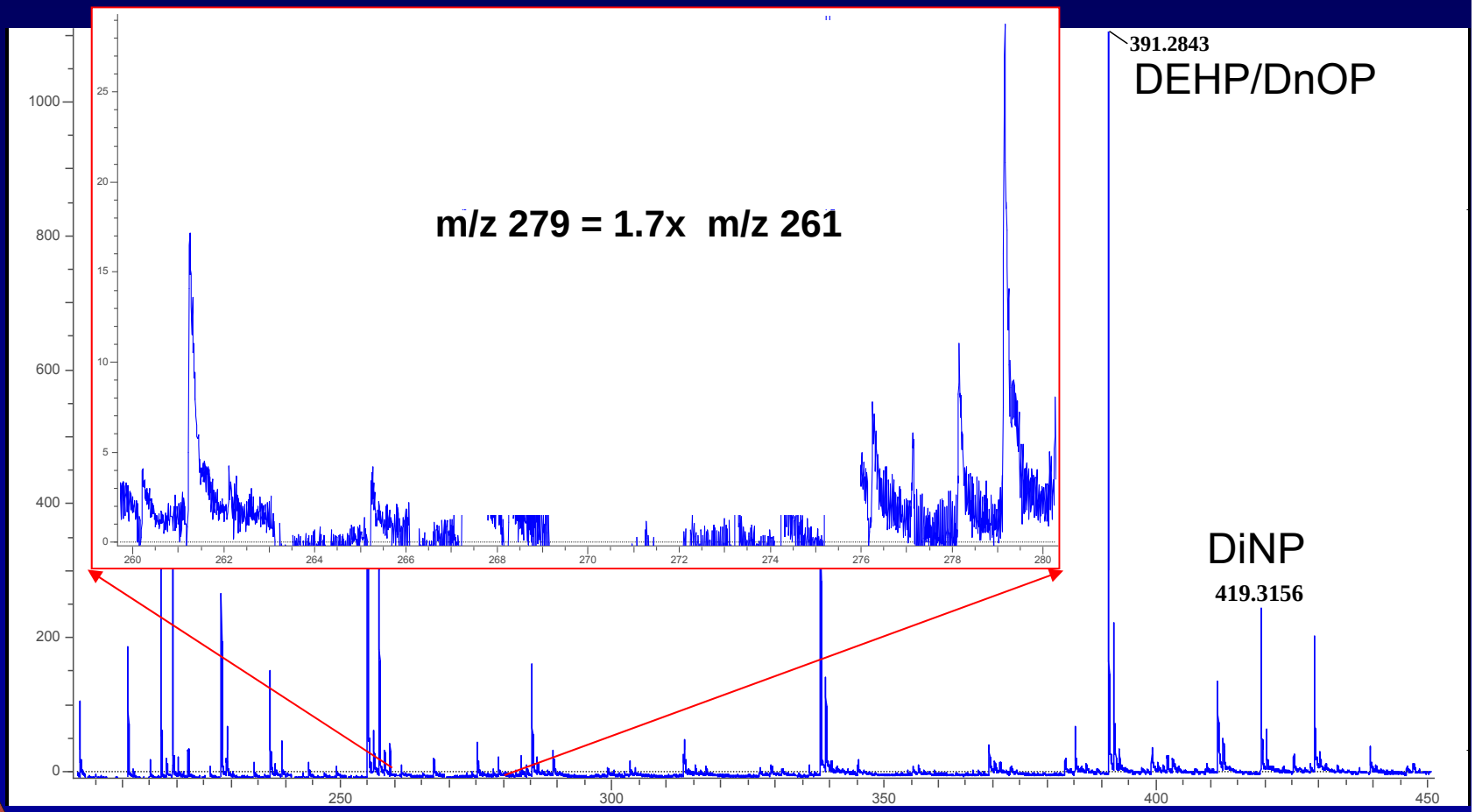

Phthalates in Food Packaging

DART-TOF

Product	Material	Part	DnOP		DEHP		DnNP		DiNP		DiDP	
			ng/cm^2	id?	ng/cm^2	id?	ng/cm^2	id?	ng/cm^2	id?	ng/cm^2	id?
Papaya Milk	Al can	exterior	-	no	mid 10's	y	-	no	low 10's	y*	-	no
Papaya Milk	Al can	interior	-	no	low 10's	y*	-	no	-	no	-	no
bean paste	foam	lid-gasket	-	no	-	no	-	no	~3000	y	-	no
bean paste	enamel	lid-metal	-	no	-	no	-	no	high100's	y	-	no
Iced Coffee	Al can	exterior	-	no	low 10's	y	-	no	<5	y**	-	no
Iced Coffee	Al can	interior	-	no	low 100's	y	-	no	mid 10's	y	-	no
Cookie Bar	flex PP m-layer	exterior	-	no	low 100's	y	-	no	low 100's	y	-	no
Cookie Bar	flex PP m-layer	interior	-	no	mid 10's	y	-	no	low 10's	y*	-	no

id = ±5mDa; & ^{13}C ±5mDa; & 2 Frag ions ±5mDa

* = frag ions too low in abund.for ±5mDa

** = frag & ^{13}C ions to low in abund for ±5mDa

LOD ~ 1ng/uL, ~1 ng/cm^2

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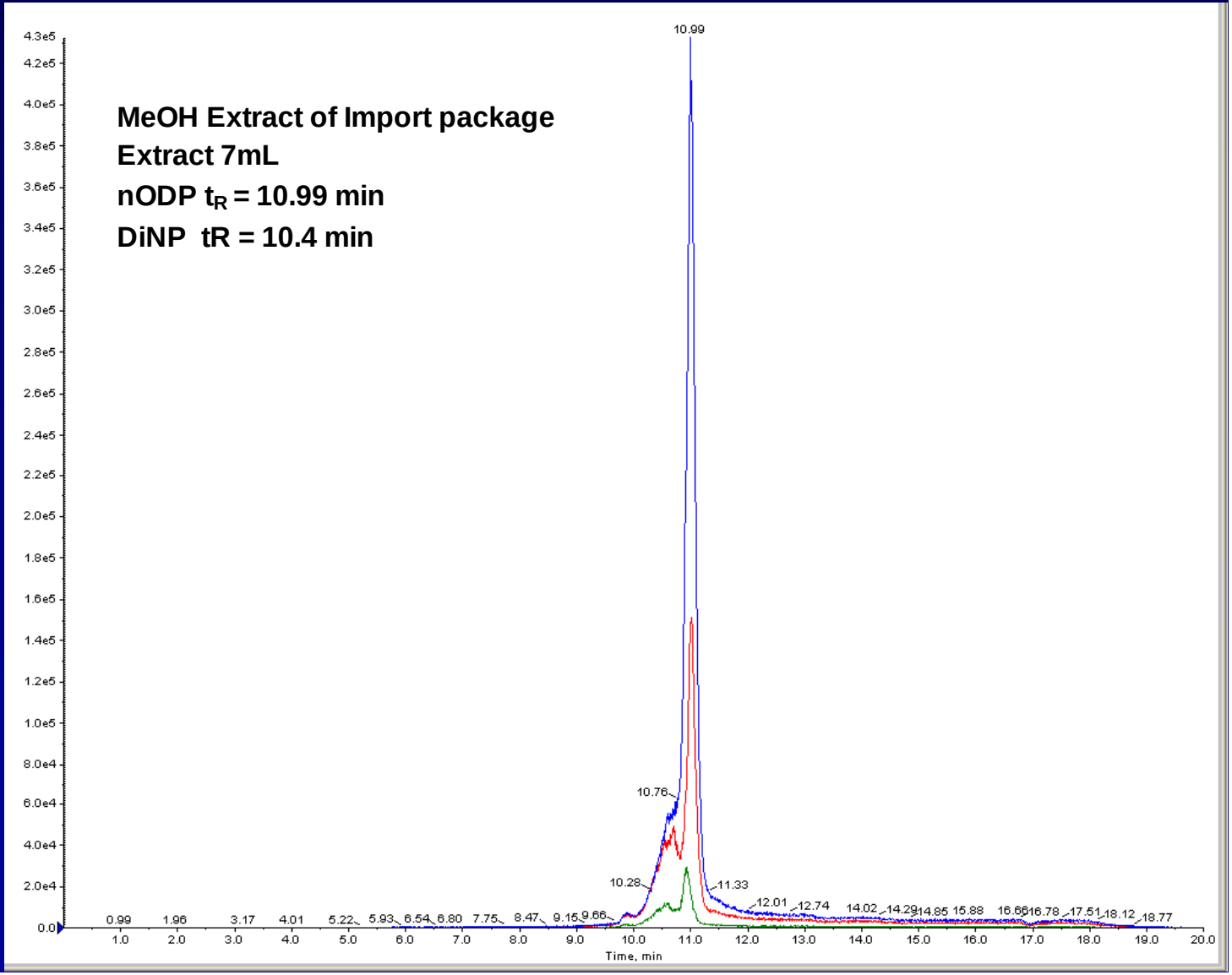
Phthalates in Food Packaging



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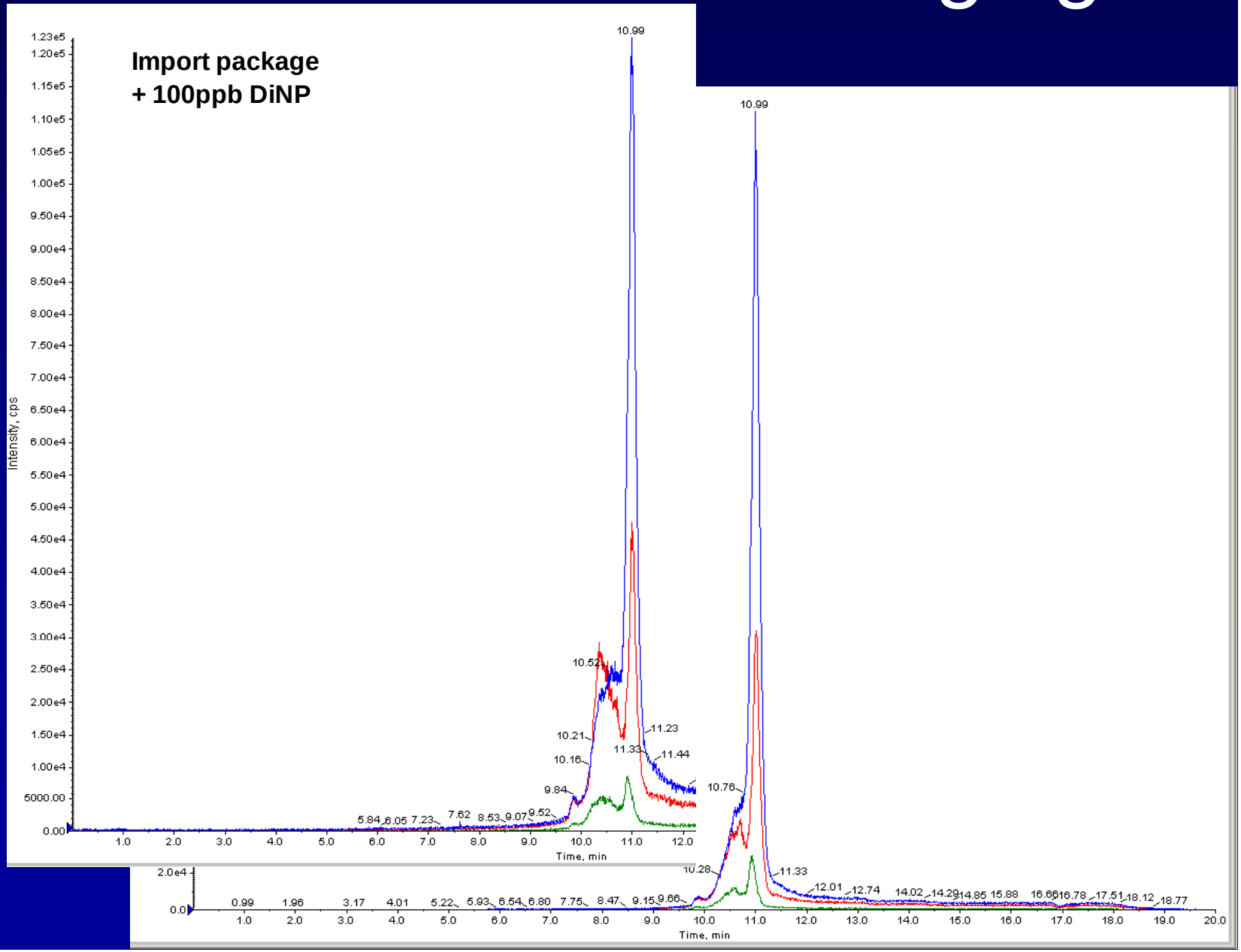

Phthalates in Food Packaging

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Product	Material	Part	DnOP		DEHP		DnNP		DiNP		DiDP	
			ng/cm^2	id?	ng/cm^2	id?	ng/cm^2	id?	ng/cm^2	id?	ng/cm^2	id?
Papaya Milk	Al can	exterior	-	no	mid 10's	y	-	no	low 10's	y*	-	no
Papaya Milk	Al can	interior	-	no	low 10's	y*	-	no	-	no	-	no
bean paste	foam	lid-gasket	-	no	-	no	-	no	~3000	y	-	no
bean paste	enamel	lid-metal	-	no	-	no	-	no	high100's	y	-	no
Iced Coffee	Al can	exterior	-	no	low 10's	y	-	no	<5	y**	-	no
Iced Coffee	Al can	interior	-	no	low 100's	y	-	no	mid 10's	y	-	no
Cookie Bar	flex PP m-layer	exterior	-	no	low 100's	y	-	no	low 100's	y	-	no
Cookie Bar	flex PP m-layer	interior	-	no	mid 10's	y	-	no	low 10's	y*	-	no

id = ±5mDa; & ^{13}C ±5mDa; & 2 Frag ions ±5mDa
* = frag ions too low in abund.for ±5mDa
** = frag & ^{13}C ions to low in abund for ±5mDa
LOD ~ 1ng/uL, ~1 ng/cm^2

LC-MS/MS

Product	Material	Part	DnOP		DEHP		DnNP		DiNP		DiDP		nODP	
			ng/cm^2	id?	ng/cm^2	id?	ng/cm^2	id?	ng/cm^2	id?	ng/cm^2	id?	ng/cm^2	id?
Cookie Bar	flex PP m-layer	exterior	~50	y	~60	y	-	no	~20	y*	-	no	~125	y
Cookie Bar	flex PP m-layer	interior	na	na	na	na	na	na	na	na	na	na	na	na

id = rt ±0.05m, 2-MRMs, stand.additions
* = MRM rel. abund varied, peak broad

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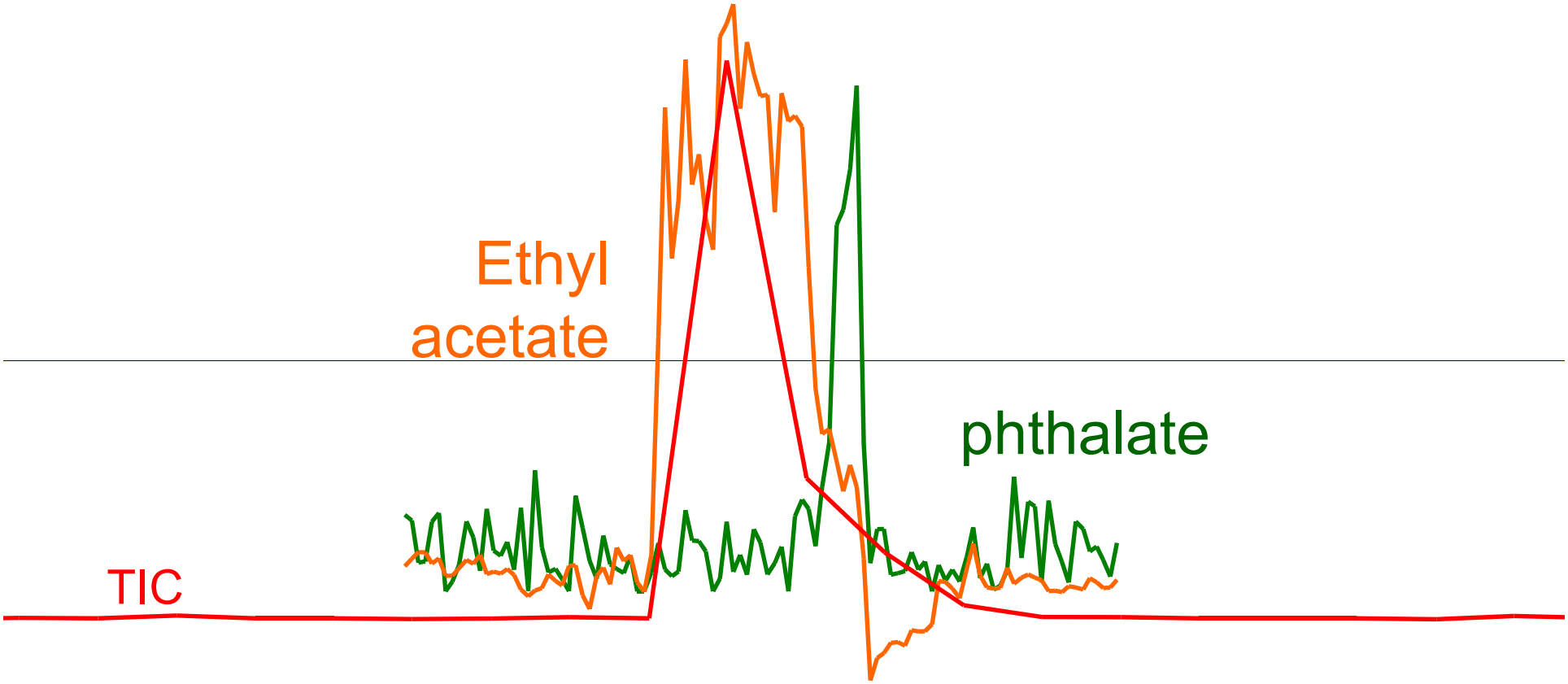
DART-MS Assessment

- DART-Sample positioning affects signal
- DART-MS more than sensitive enough (phthalates)
- DART-MS can be quant/semi-quant…w/IS in solvent
- DART-MS can be semi-quant off polymer surfaces
- DART-MS can not reliably identify phthalates isomers in isomeric mixtures.

FDA CFSAN

DART-MS parameter's effects