Application of gas chromatography atmospheric pressure chemical ionization mass spectrometry for analysis of contaminants in environmental samples

PETR KUKUČKA[1,2]; ONDŘEJ AUDY[1], DAWEI GENG[2], JORDAN STUBLESKI[2], INGRID ERICSON JOGSTEN[2], JANA KLÁNOVÁ[1]

[1] RECETOX, Masaryk University, Kamenice 5, 62500 Brno, Czech Republic, kukucka@recetox.muni.cz

[2] MTM, School of Science and Technology, Örebro University, 701 82 Örebro, Sweden

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Outline

- GC-APCI-MS (background)
- selected applications
- user experience

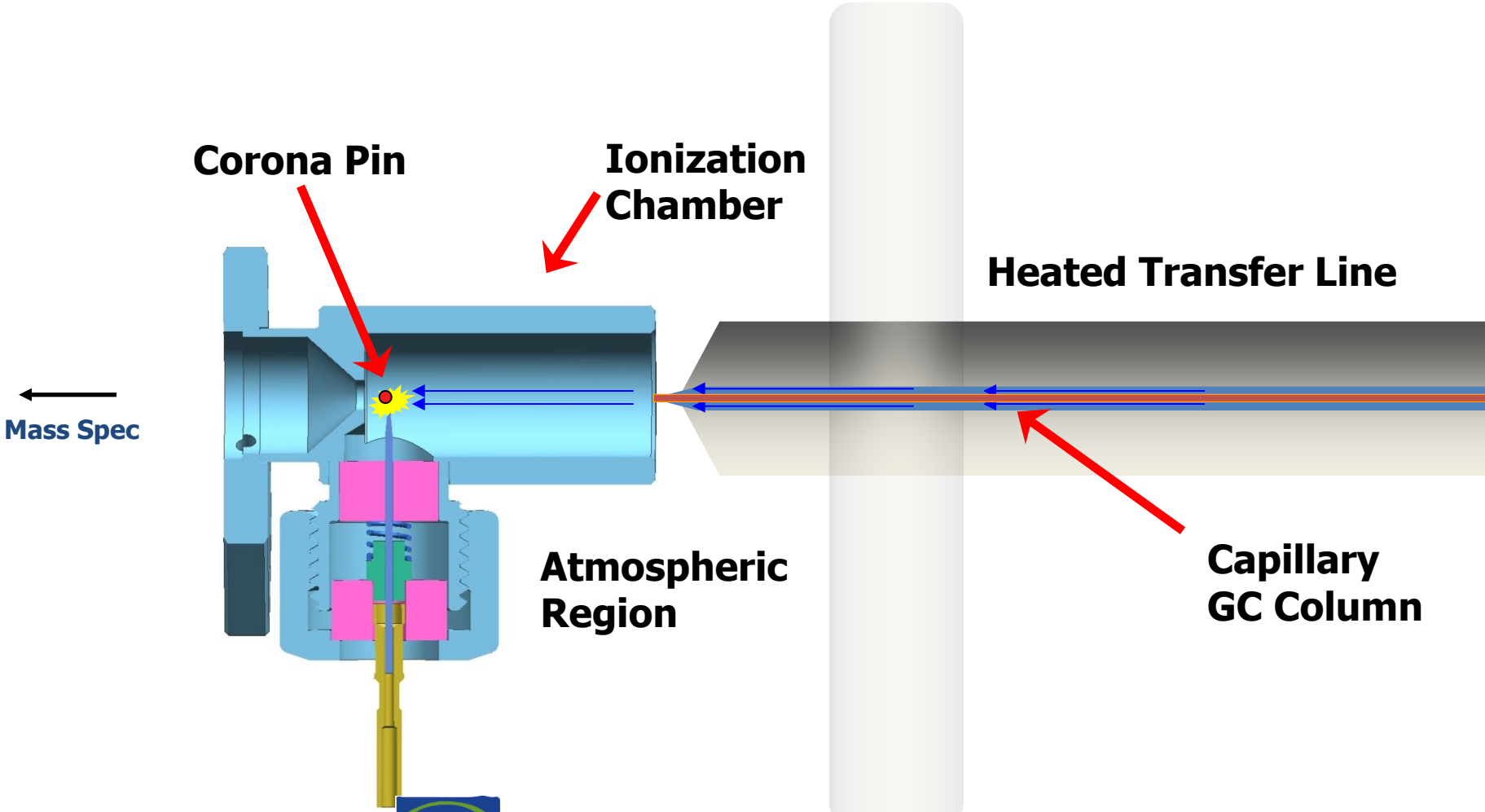
GC-APCI-MS background

- Atmospheric Pressure Chemical Ionisation in Gas Chromatography-Mass Spectrometry
- optional ion source for MS systems to provide sensitive GC-MS, MS/MS & HRMS capability

- ionisation by APCI is soft and molecular ions should be readily detected – possibility for tandem mass spectrometry
- easy to switch between GC and LC inlets on MS systems (or other ion source) without venting

- system: Agilent 7890 GC soupled to Waters Xevo TQ-S MS, APGC source

GC-APCI-MS background



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GC-APCI-MS background

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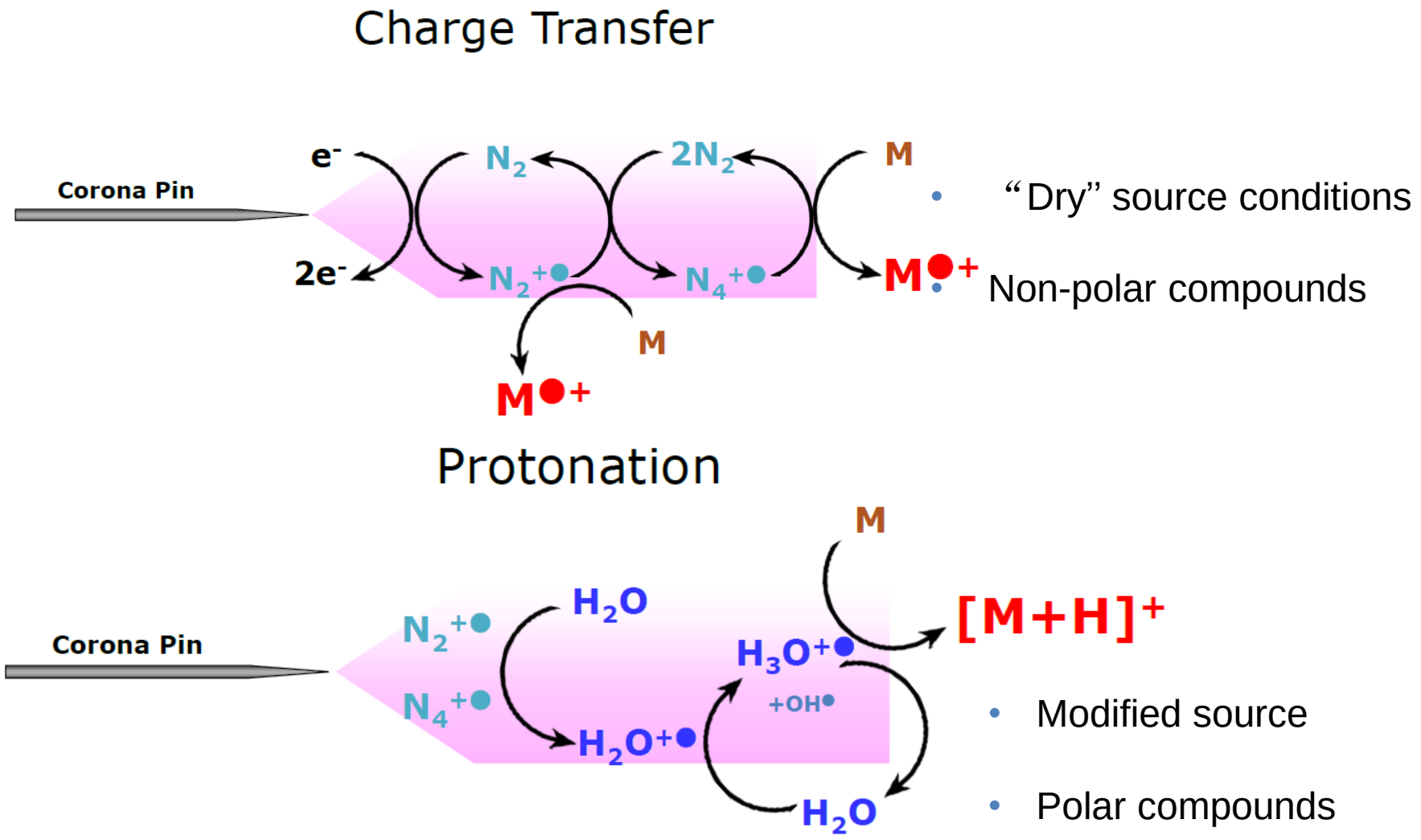
GC-APCI-MS Ionization

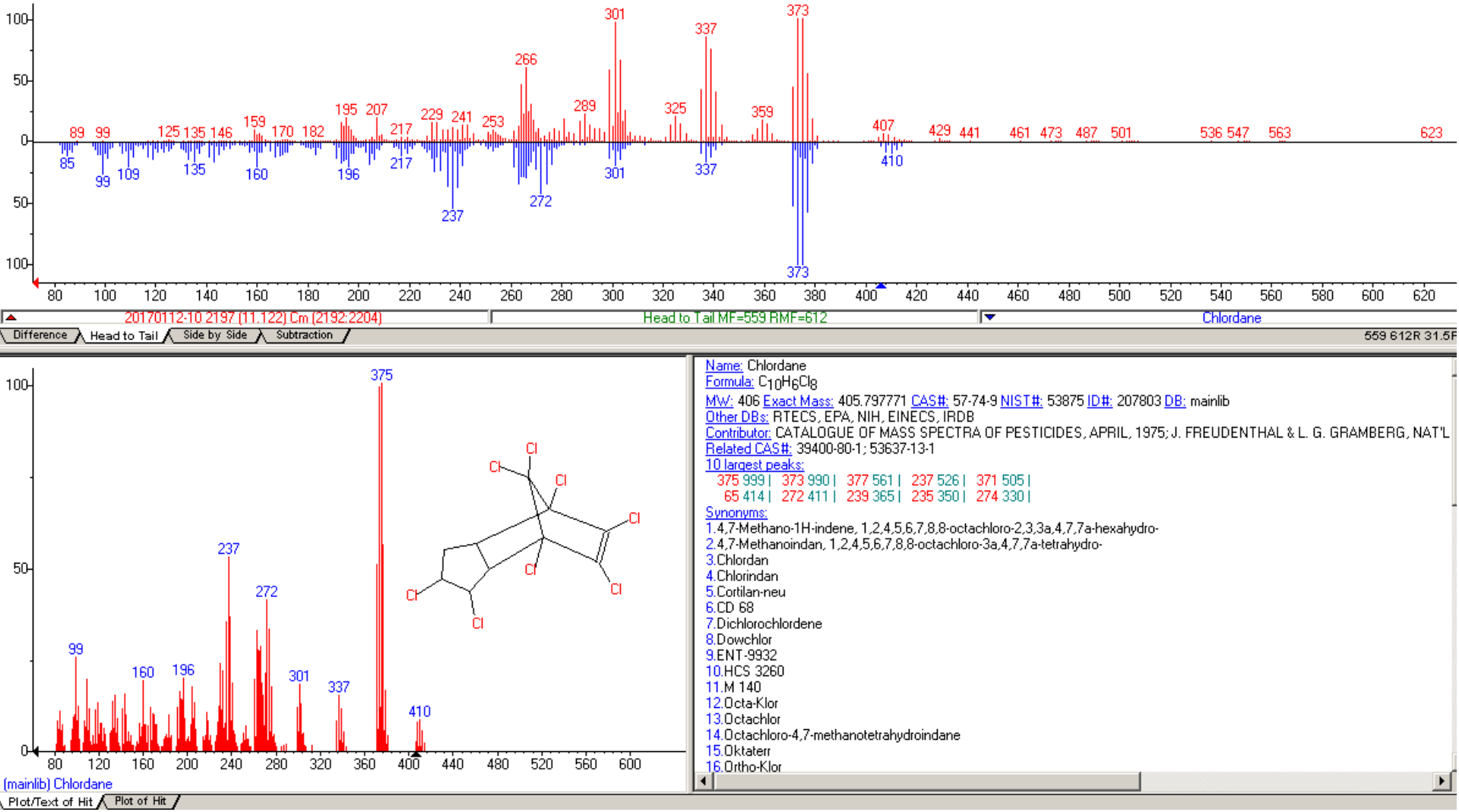


Applications: drin pesticides

- larger group of selected organochlorine pesticides
- many being phased out, but residues are still present in the environment
- various national and international regulations on use and limits set in food safety

- GC-EI-MS: strong fragmentation, often providing same major fragments
- GC-NCI-MS: favorable, but need of use of reagent gas, ion source getting dirty fast

Applications: drin pesticides



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Applications: drin pesticides

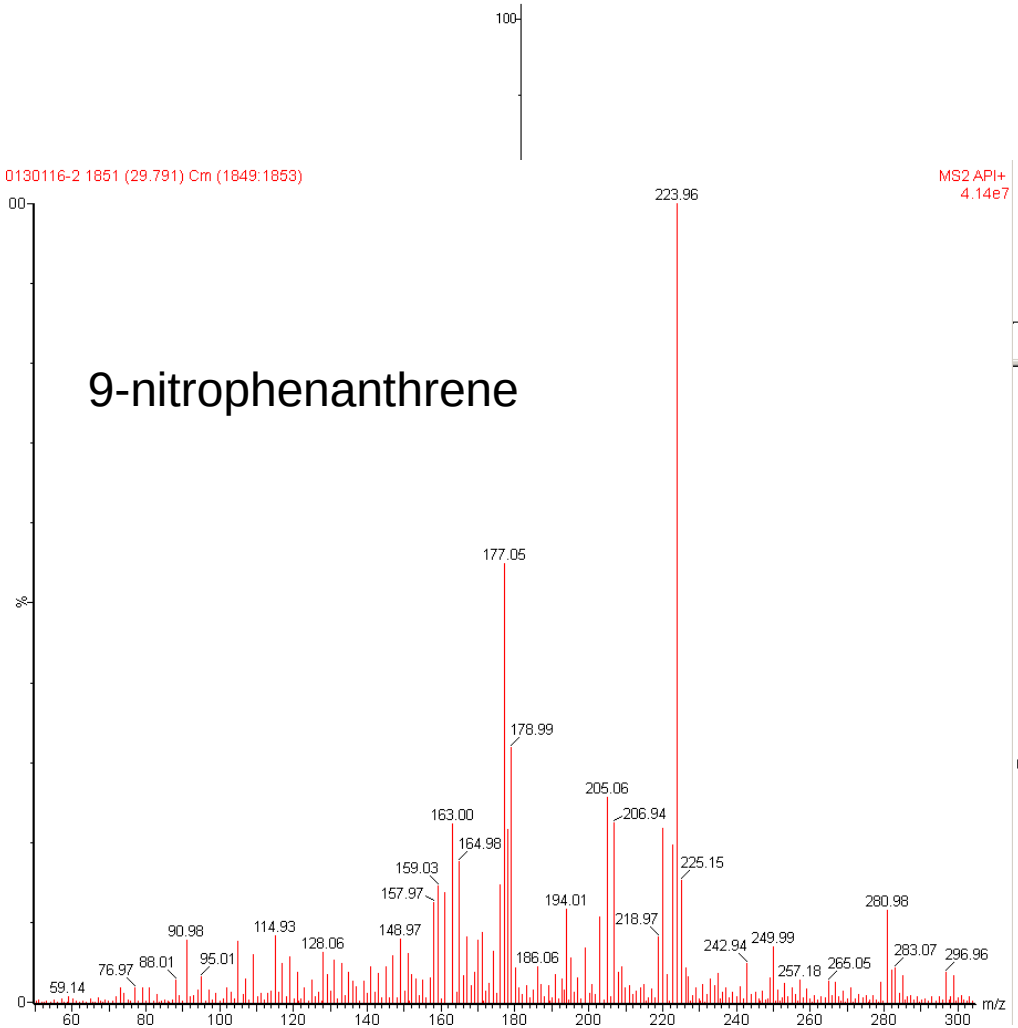
compound	range	MRM1	MRM2	LOQ (pg on-column)	R^2
heptachlor	1-1000 pg/uL	336.7 > 265.8	338.7 > 267.8	0.073	0.999
heptachlor epoxide (A)	1-1000 pg/uL	352.7 > 252.8	354.7 > 252.8	0.475	0.997
heptachlor epoxide (B)	1-1000 pg/uL	352.7 > 252.8	354.7 > 252.8	0.256	0.999
aldrin	1-1000 pg/uL	262.7 > 227.8	260.7 > 225.8	0.035	0.999
dieldrin	1-1000 pg/uL	382.7 > 278.8	380.7 > 278.8	0.044	0.999
endrin	1-1000 pg/uL	381.7 > 280.9	379.7 > 280.9	0.088	0.999
endrin aldehyde	1-1000 pg/uL	380.7 > 280.8	382.7 > 280.8	0.405	0.999
endrin ketone	1-1000 pg/uL	380.7 > 244.8	382.7 > 245.8	0.120	0.999
isodrine	1-1000 pg/uL	365.7 > 195	363.7 > 193	0.009	0.999
oxychlordane	1-1000 pg/uL	388.7 > 288.8	386.7 > 286.8	0.114	0.996
g-chlordane	1-1000 pg/uL	374.7 > 265.8	372.7 > 265.8	0.020	0.999
a-chlordane	1-1000 pg/uL	374.7 > 265.8	372.7 > 265.8	0.020	0.998
a-endosulfan	1-1000 pg/uL	407.8 > 252.8	406.8 > 252.8	0.223	0.998
b-endosulfan	1-1000 pg/uL	407.8 > 252.8	406.8 > 252.8	0.218	0.999
endosulfan sulfate	1-1000 pg/uL	421.8 > 228.8	423.8 > 228.8	0.041	0.999
methoxychlor	1-1000 pg/uL	228 > 169	227 > 212	0.022	0.999
mirex	1-1000 pg/uL	271.8 > 236.8	270.8 > 236.8	0.003	0.999

Applications: PAHs derivates (nitro-, oxy-)

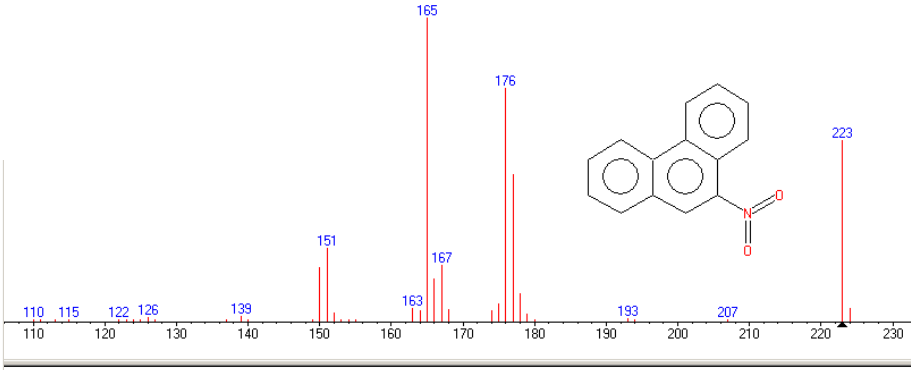
- ubiquitous persistent environmental pollutants, 2 and more condensed aromatic rings
- different structures – linear, clusters, angular, derivates (alkyl-, nitro-, hydroxy-, oxy- …), heteroatoms (S, N)
- classified as priority pollutants by US EPA (16 indicator compounds)
- adverse toxic effect on living organisms, many are potential carcinogens, BaP classified as Group 1 human carcinogen (IARC)
- long environmental half lives, on going sources (combustion, traffic), atmospheric reactions

- GC-EI-MS: possible interference with native PAHs
- GC-NCI-MS: favorable, in NCI disadvantageous MS/MS as the freagment is NO_2-

Applications: PAHs derivates (nitro-, oxy-)



9-nitrophenanthrene



phenanthrene, *Sci. Total Environ.*, *148*, **1994**, 11-21.

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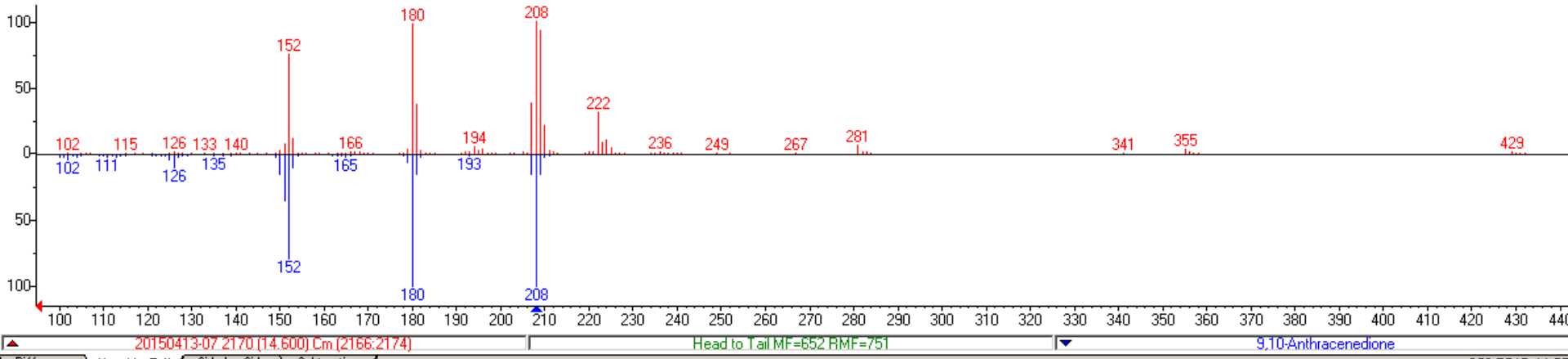
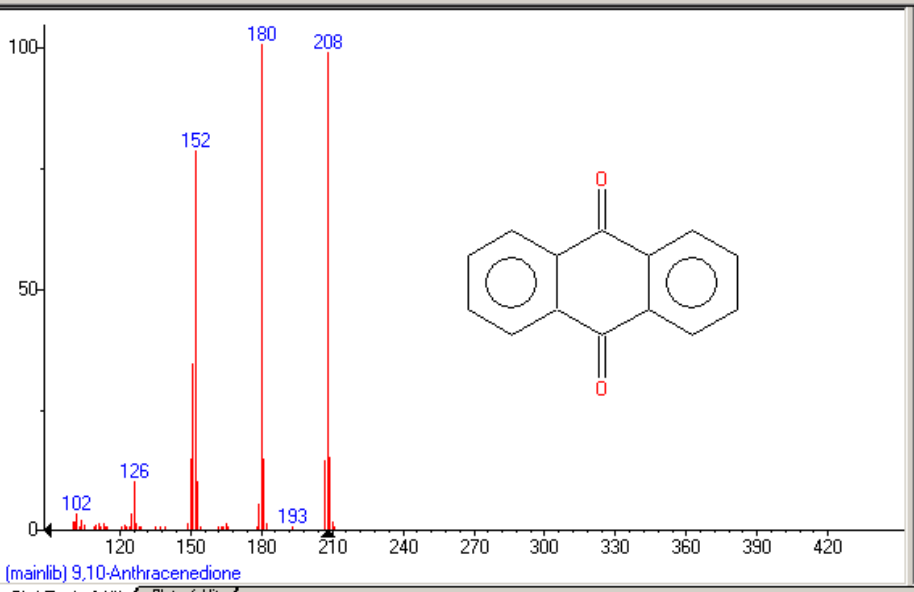
Applications: PAHs derivates (nitro-, oxy-)





Name: 9,10-Anthracenedione
Formula: $C_{14}H_8O_2$
MW: 208 Exact Mass: 208.052429 CAS#: 84-65-1 NIST#: 152564 ID#: 148126 DB: mainlib
Other DBs: Fine, TSCA, RTECS, EPA, HODOC, NIH, EINECS, IRDB
Contributor: Chemical Concepts
Related CAS#: 790240-52-7
10 largest peaks:
180 999 | 208 983 | 152 780 | 76 442 | 151 339 |
50 194 | 75 166 | 209 148 | 150 146 | 181 144 |
Synonyms:
1.Anthraquinone
2.Anthradione
3.Hoelite
4.Morkit
5.9,10-Anthraquinone
6.Anthracene, 9,10-dihydro-9,10-dioxo-
7.9,10-Dioxoanthracene
8.9,10-Anthrachinon
9.Corbit
10.Anthracene-9,10-quinone
11.Anthra-9,10-quinone #
12.NSC 7957

Estimated non-polar retention index (n-alkane scale):
Value: 1956 iu
Confidence interval (Ketones): 57(50%) 246(95%) iu

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Applications: nitroPAHs

compound	range	MRM1	MRM2	LOQ (pg on-column)	R^2
1-nitronaphthalene	0.1-100 pg/uL	174 > 127	173 > 145	0.076	0.999
2-nitronaphthalene	0.1-100 pg/uL	173 > 127	174 > 127	0.007	0.999
3-nitroacenaphthene	0.1-100 pg/uL	200 > 153	199 > 169	0.032	0.999
5-nitroacenaphthene	0.1-100 pg/uL	199 > 169	200 > 153	0.004	0.997
2-nitrofluorene	0.1-100 pg/uL	211 > 164	212 > 195	0.033	0.994
9-nitroanthracene	0.1-100 pg/uL	223 > 193	223 > 178	0.034	0.999
9-nitrophenanthrene	0.1-100 pg/uL	223 > 167	223 > 178	0.013	0.999
3-nitrophenanthrene	0.1-100 pg/uL	223 > 176	223 > 193	0.025	0.999
2-nitrofluoranthene	0.1-100 pg/uL	247 > 201	248 > 202	0.005	0.999
3-nitrofluoranthene	0.1-100 pg/uL	247 > 217	247 > 189	0.008	0.999
1-nitropyrene	0.1-100 pg/uL	247 > 217	247 > 201	0.006	0.999
2-nitropyrene	0.1-100 pg/uL	247 > 201	248 > 202	0.004	0.999
7-nitrobenzo(a)anthracene	0.1-100 pg/uL	273 > 215	274 > 257	0.014	0.999
6-nitrochrysene	0.1-100 pg/uL	273 > 215	274 > 226	0.008	0.999
1,3-dinitropyrene	0.1-100 pg/uL	292 > 188	292 > 176	0.009	0.999
1,6-dinitropyrene	0.1-100 pg/uL	292 > 176	292 > 232	0.024	0.998
1,8-dinitropyrene	0.1-100 pg/uL	292 > 176	292 > 232	0.010	0.998
6-nitrobenzo(a)pyrene	0.1-100 pg/uL	297 > 239	297 > 224	0.006	0.999

Applications: oxyPAHs

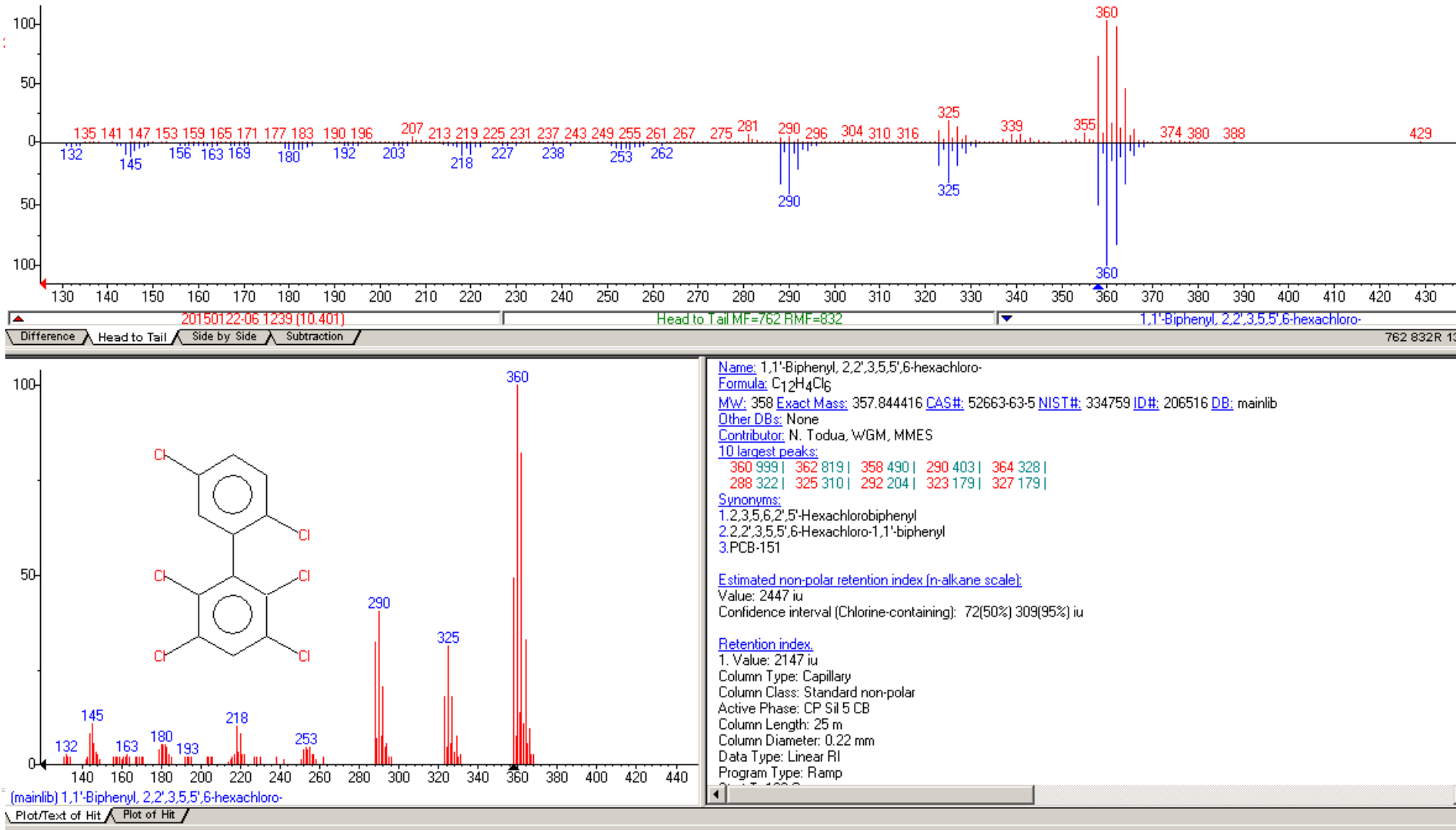
compound	range	MRM1	MRM2	LOQ (pg on-column)	R^2
1,4-naphthoquinone	0.1-100 pg/uL	158 > 102	159 > 103	0.049	0.999
naphthalene-1-aldehyde	0.1-100 pg/uL	156 > 128	157 > 128	0.027	0.999
9-fluorenone	0.1-100 pg/uL	180 > 152	181 > 153	0.010	0.994
9,10-anthraquinone	0.1-100 pg/uL	208 > 152	209 > 153	0.015	0.999
1,4-anthraquinone	0.1-100 pg/uL	208 > 152	209 > 153	0.011	0.999
benzo-a-fluoren-11-one	0.1-100 pg/uL	230 > 202	231 > 203	0.013	0.999
benzo-b-fluoren-11-one	0.1-100 pg/uL	230 > 202	231 > 203	0.012	0.999
benzanthrone	0.1-100 pg/uL	230 > 202	231 > 203	0.009	0.999
benzo(a)anthracene-7,12-dione	0.1-100 pg/uL	258 > 202	259 > 203	0.010	0.997
5,12-naphthacenequinone	0.1-100 pg/uL	258 > 202	259 > 203	0.010	0.999

Applications: PCBs and OCPs

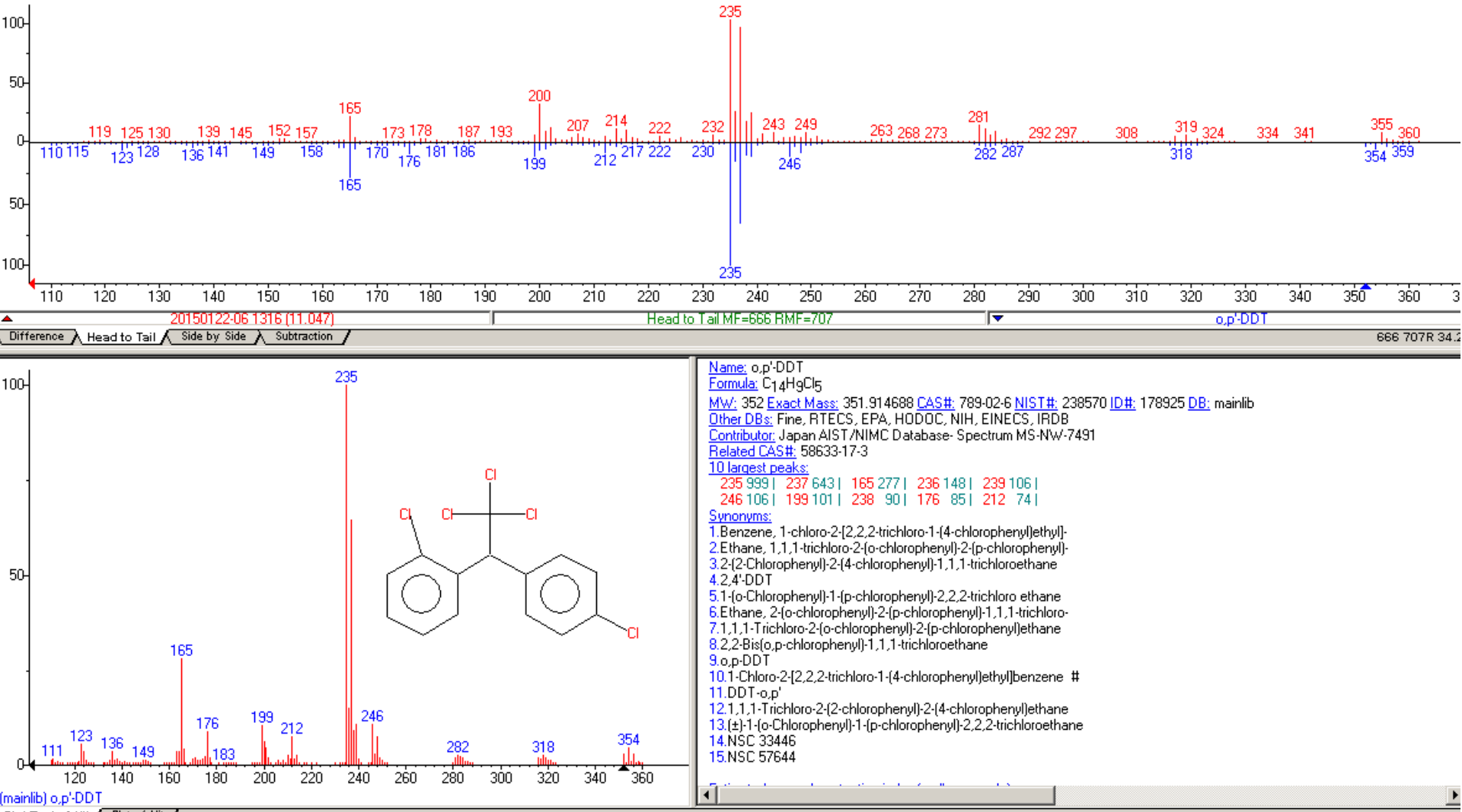
- legacy anthropogenic compounds, ubiquitous in the environment
- various national and international regulations
- seasonal cycling in atmosphere, global transport toward colder regions (polar)

- GC-EI-MS: commonly used, acceptable detection limits
- GC-NCI-MS: provides lower detection and quantitation limits

Applications: PCBs and OCPs



Applications: PCBs and OCPs



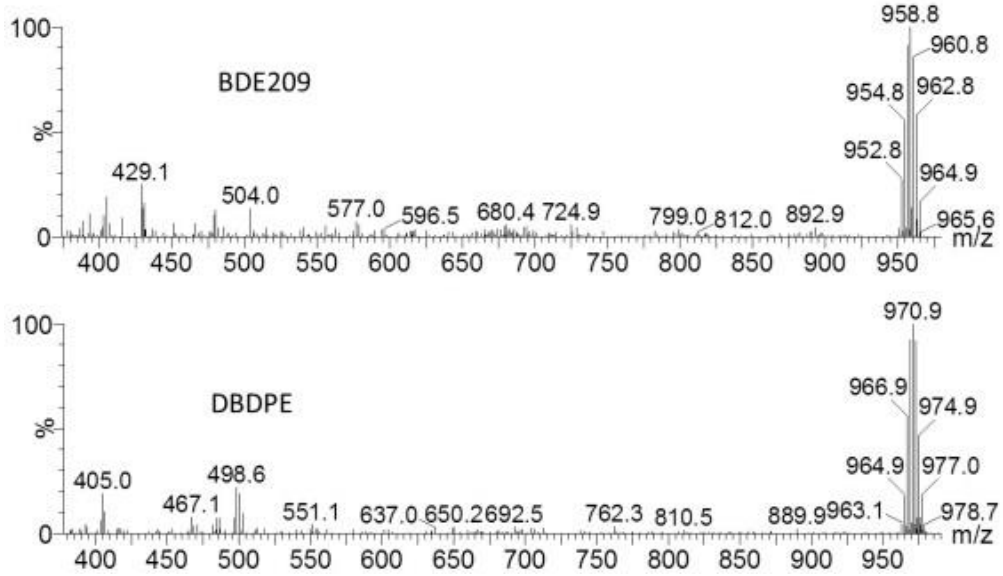
Applications: PCBs and OCPs

compound	range	MRM1	MRM2	LOQ (pg on-column)	RRF RSD%
PCB 28	0.1-400 pg/uL	255.9 > 185.9	257.9 > 185.9	0.003	12.245
PCB 52	0.1-400 pg/uL	289.8 > 219.9	291.9 > 221.9	0.002	10.037
PCB 101	0.1-400 pg/uL	325.8 > 255.8	327.8 > 255.8	0.006	11.302
PCB 118	0.1-400 pg/uL	325.8 > 255.8	327.8 > 255.8	0.009	12.445
PCB 153	0.1-400 pg/uL	359.7 > 289.8	361.7 > 289.8	0.006	11.729
PCB 138	0.1-400 pg/uL	359.7 > 289.8	361.7 > 289.8	0.007	12.258
PCB 180	0.1-400 pg/uL	393.6 > 323.7	395.6 > 325.7	0.003	11.293
PeCB	0.1-400 pg/uL	247.8 > 212.8	251.8 > 216.8	0.004	10.931
HCB	0.1-400 pg/uL	283.7 > 248.7	285.7 > 250.7	0.008	16.218
a-HCH	0.1-400 pg/uL	216.8 > 144.8	218.8 > 146.8	0.073	14.397
b-HCH	0.1-400 pg/uL	216.8 > 144.8	218.8 > 146.8	0.086	26.557
c-HCH Lindane	0.1-400 pg/uL	216.8 > 144.8	218.8 > 146.8	0.077	20.114
d-HCH	0.1-400 pg/uL	216.8 > 144.8	218.8 > 146.8	0.102	12.815
e-HCH	0.1-400 pg/uL	216.8 > 144.8	218.8 > 146.8	0.158	10.581
o,p'-DDE	0.1-400 pg/uL	317.8 > 245.9	319.8 > 247.9	0.005	12.159
p,p'-DDE	0.1-400 pg/uL	317.8 > 245.9	319.8 > 247.9	0.006	10.532
o,p'-DDD	0.1-400 pg/uL	234.9 > 165	236.9 > 165	0.012	15.967
p,p'-DDD	0.1-400 pg/uL	234.9 > 165	236.9 > 165	0.013	18.776
o,p'-DDT	0.1-400 pg/uL	234.9 > 165	236.9 > 165	0.016	15.099
p,p'-DDT	0.1-400 pg/uL	234.9 > 165	236.9 > 165	0.016	15.246

Applications: PBDEs

- flame retardants present in electronics and furnishing
- obsolete, but still present in environment

- GC-EI-MS: commonly used, acceptable detection limits
- GC-NCI-MS: provides lower detection and quantitation limits



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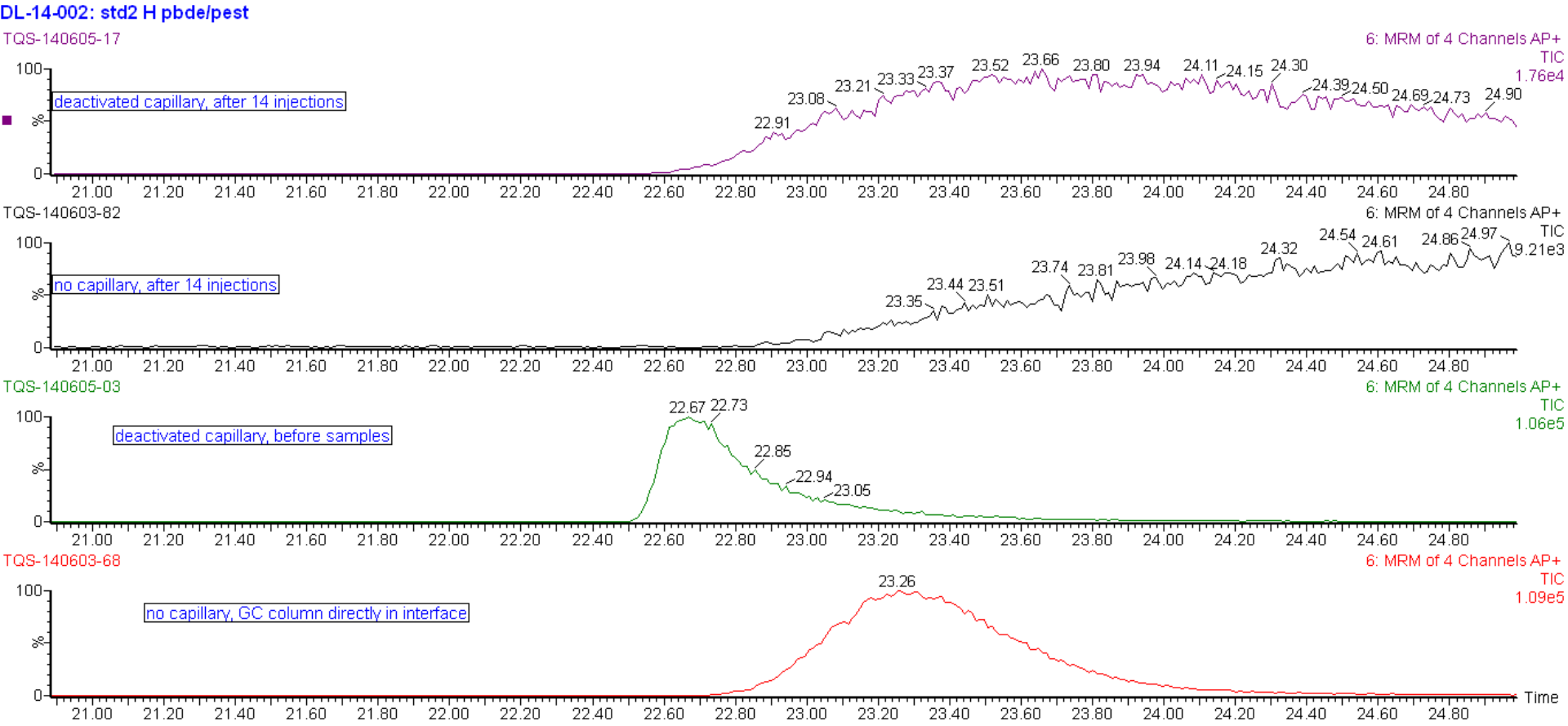
GC-APCI-MS, decaBDE separation



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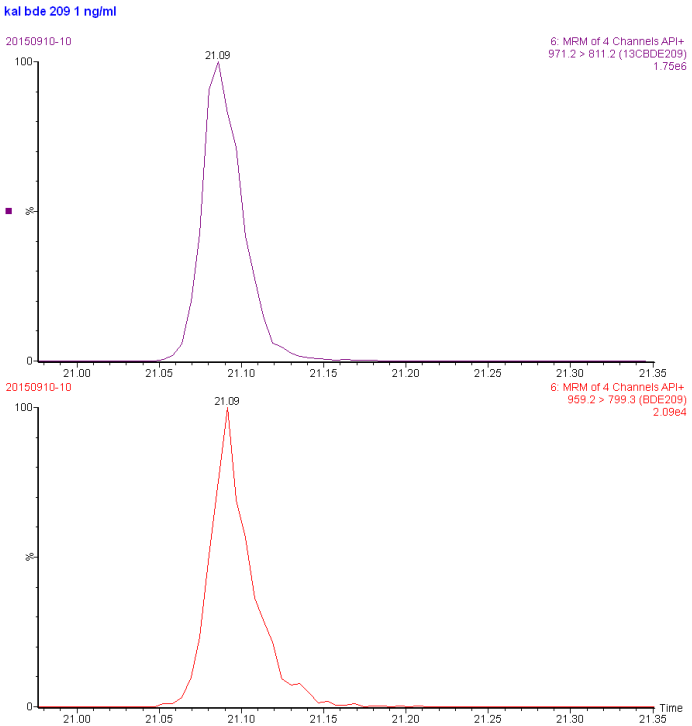
GC-APCI-MS early version issues

- uneven heat distribution in the transfer line, causing late eluting (high boiling point) compounds to broaden peaks
- charred outer layer (polyimide) of capillary columns – charred particles”getting through source into analyzer
- selected BDE209 as benchmark compound for transfer line tests
- need to use high interface temperatures (350°C or higher)
- tested selected available capillaries (length ~80 cm) in the interface

GC-APCI-MS early version issues

- deactivated capillary – no improvement
- Siltek (Restek) coated high temperature capilalry – improvement, but after some time the outer layer is still getting charred
- Ultimetal tubing (Agilent) with ultimate metal unions – so far the best solution – long lifetime, no charring



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Applications: PBDEs

compound	range	MRM1	MRM2	LOQ (pg on-column)	RRF RSD%
BDE 28	0.1-100 pg/uL	407.8 > 248	405.8 > 246	0.0003	6.987
BDE 47	0.1-100 pg/uL	485.7 > 325.8	483.7 > 325.8	0.0016	10.493
BDE 66	0.1-100 pg/uL	485.7 > 325.8	483.7 > 325.8	0.0018	12.318
BDE 100	0.1-100 pg/uL	563.6 > 403.7	565.6 > 405.7	0.0012	11.524
BDE 99	0.1-100 pg/uL	563.6 > 403.7	565.6 > 405.7	0.001	9.366
BDE 85	0.1-100 pg/uL	563.6 > 403.7	565.6 > 405.7	0.0013	9.007
BDE 154	0.1-100 pg/uL	643.5 > 483.6	641.5 > 481.6	0.0047	11.86
BDE 153	0.1-100 pg/uL	643.5 > 483.6	641.5 > 481.6	0.0054	9.751
BDE 183	0.1-100 pg/uL	723.4 > 563.6	721.4 > 561.7	0.0057	13.776
BDE 209	1-1000 pg/uL	959.2 > 799.3	961.2 > 801.3	0.004	18.903

Applications: PBDEs, Interlab results

PBDE – Air extract (TOL)

Region	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG
Air extract (TOL)											
PBDE											
BDE 17	-0.08	NA	-0.38	NA	-0.83	1.16	NA	0.75	NA	NA	NA

PBDE – Sediment

Region	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG
Sediment											
PBDE											
BDE 47	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE 99	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE 100	1.45	NA	NA	NA	NA	-0.74	NA	-0.04	NA	NA	-1.30
BDE 153	1.00	NA	NA	NA	NA	NA	NA	NA	NA	NA	-0.74
BDE 154	0.91	NA	NA	NA	NA	-1.02	NA	NA	NA	NA	-0.33
BDE 183	0.22	NA	NA	NA	NA	6.72	NA	NA	NA	NA	-0.76
Sum PBDE Lower Bound (ND=0)	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*
Sum PBDE Upper Bound (ND=LOD)	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*

GC-APCI-MS Summary

- promising technique providing good detection and quatitation limits
- favorable use in combination with tandem mass spectrometry for targeted analysis
- good linearity of responses, ease of use
- provides good accuracy for quantification
- robust technique after solving interface issues

Acknowledgement

- Czech Ministry of Education, Youth and Sports (LO1214 and LM2015051)
- China Scholarship Council (Grant No. 201206400003)
- Jack Cochran (Restek, formerly)
- Frank Dorman (Pennsylvania State University)

Thank you for attention

kukucka@recetox.muni.cz