



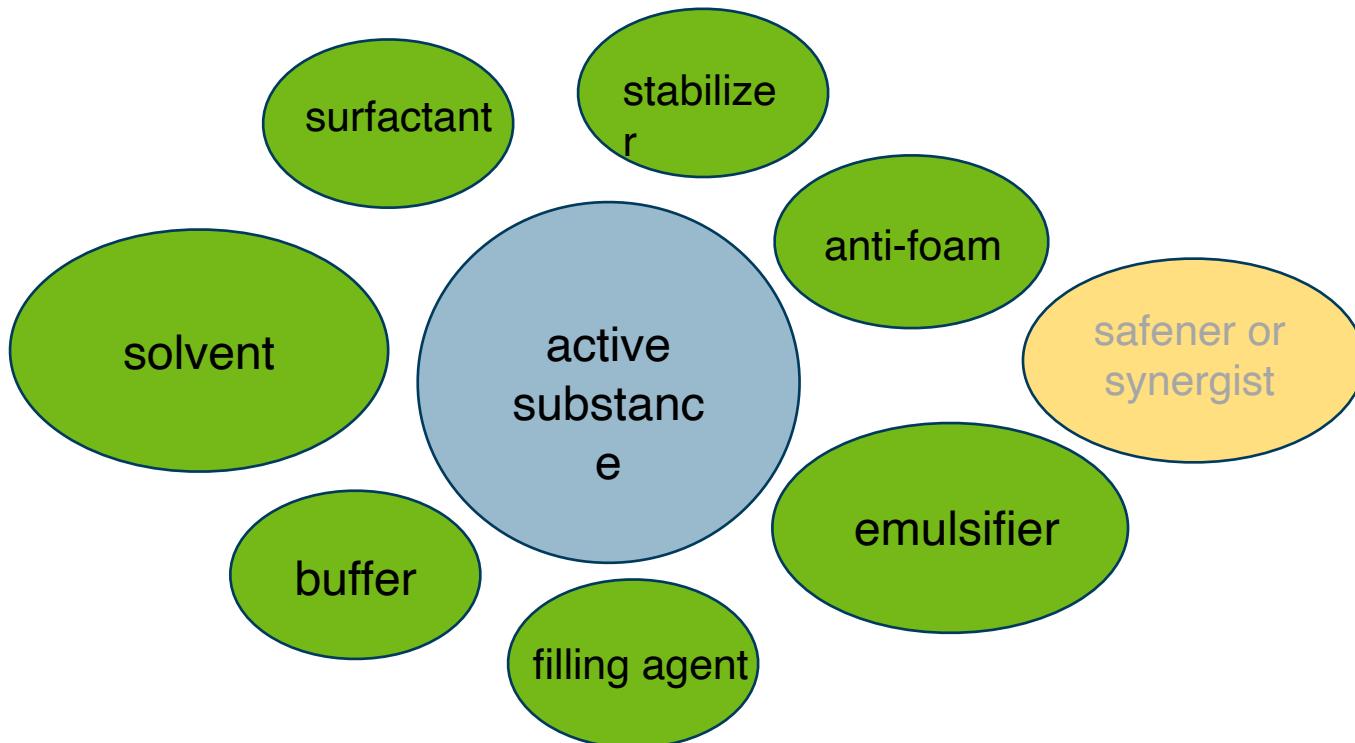
Analysis of solvent naphtha formulants in plant protection products

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Plant Protection Products – composition

A plant protection products consists of

- one or more active ingredients
- a safener or synergist
- co-formulants, consisting of one or more co-formulant substances





History

- before 1970: authorisation only on national level
- 1978: Council Directive 79/117/EEC of the European Economic Community
first ban of definite substances in PPPs
 - mercuric(organic) substances, persistent organic chlorine compounds

→ implementation in national law: Plant protection use regulation (DE)
- 1991: Council Directive 91/414/EEC concerning the placing of plant protection products on the market
- Before 2009 only in special cases requirements for co-formulants,
e.g., tallow amines and NPE
- 2009: Regulation (EC) No 1107/2009
repealing both Council Directives of EEC
 - explicit requirements also for co-formulants, e.g., annex III



Evaluation – Body of laws

Commission regulation
(EU) 284/2013
data requirements PPP

Implementing regulation
(EU) 2023/574
detailed rules unacceptable
co-formulants

Regulation (EC) 1107/2009
placing of plant protection
products on the market

Commission regulation
(EU) 283/2013
data requirements active subs.

Body of laws for
evaluation

Regulation (EC)
1272/2008
CLP regulation

Regulation (EC) No
1907/2006
REACH regulation

Annex III Regulation (EU)
2021/383
unacceptable co-formulants

National Plant
Protection law



Unacceptable co-formulants– Annex III

of Reg. (EG) 1107/2009

Article 27

(1) A co-formulant shall not be accepted for inclusion in a plant protection product where it has been established that:

- (a) its residues, consequent on application consistent with good plant protection practice, and having regard to realistic conditions of use, have a harmful effect on human or animal health or on groundwater or an unacceptable effect on the environment; or
- (b) its use, consequent on application consistent with good plant protection practice and having regard to realistic conditions of use, has a harmful effect on human or animal health or an unacceptable effect on plants, plant products or the environment.



Unacceptable co-formulants – Annex III of Reg. (EG) 1107/2009

Cut off criteria for co-formulants

**CLP Reg.
1272/2008**

carcinogen cat. 1A/1B
mutagen cat. 1A/1B
toxic carcinogen
to reproduction
cat. 1A /1B

**REACH Reg.
1907/2006**

(very) persistent
(very) bioaccumulative
toxic
(PBT/ VPvB)
endocrine disruptors

Reg. 850/2004

persistent organic
pollutants (POP)

- narrow 2000 different co-formulants in authorised PPPs
- currently **144** entries in the list of unacceptable co-formulants (Annex III)



Solvent naphtha co-formulants

Use

- solvent
- surfactant
- emulsifier
- mostly in suspension concentrates, emulsion concentrates
- Production via fractional mineral oil distillation
- Differentiation via boiling point areas

example:

Solvesso 100: bp 154 °C – 174 °C (C_9, C_{10})

Solvesso 150: bp 175 °C – 200 °C (C_{10}, C_9)

Solvesso 200: bp above 200 °C ($C_{11}, C_{12}, C_{13}, C_{14}$)

Trade names, examples

- Solvesso
- Hydrosol
- Shellsol
- Caromax



Solvent naphtha co-formulants - requirements

Development

Regulation (EC) No 1272/2008 (CLP)

- in force since 20.01.2009
- classification of naphthalene as carcinogen cat. 2
- labelling obligation at contents $\geq 1\%$

Delegated regulation (EU) 692/2022

- in force since 23.11.2023
- amending of Regulation (EC) 1272/2008
- classification of cumene as carcinogen cat. 1B
- labelling obligation at contents $\geq 0,1\%$



Solvent naphtha co-formulants - composition

Example boiling point 200 °C and higher

Without purification

- naphthalene < 10%
- cumene not listed

Naphthalene depleted

- naphthalene < 1%
- cumene not listed

Further purification (since 2023)

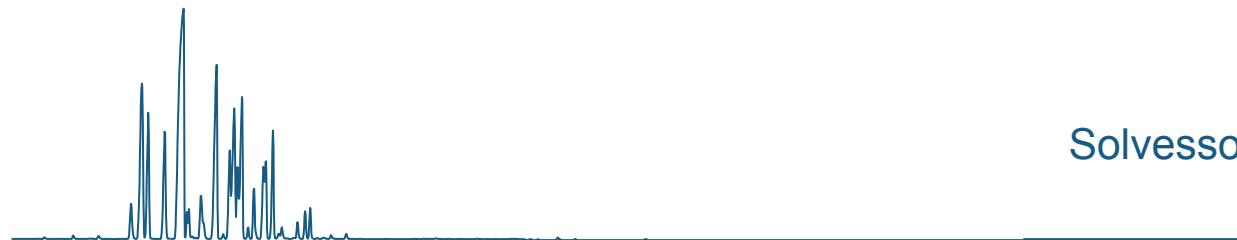
- naphthalene < 1%
- cumene < 0,0005%



Solvent naphtha co-formulants - 2014

ND = Naphthalene-depleted

Trimethylbenzene

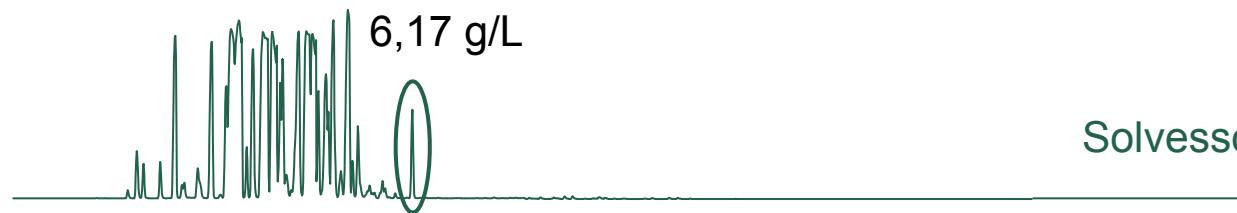


Solvesso 100

Naphthalene

Boiling point: 218 °C

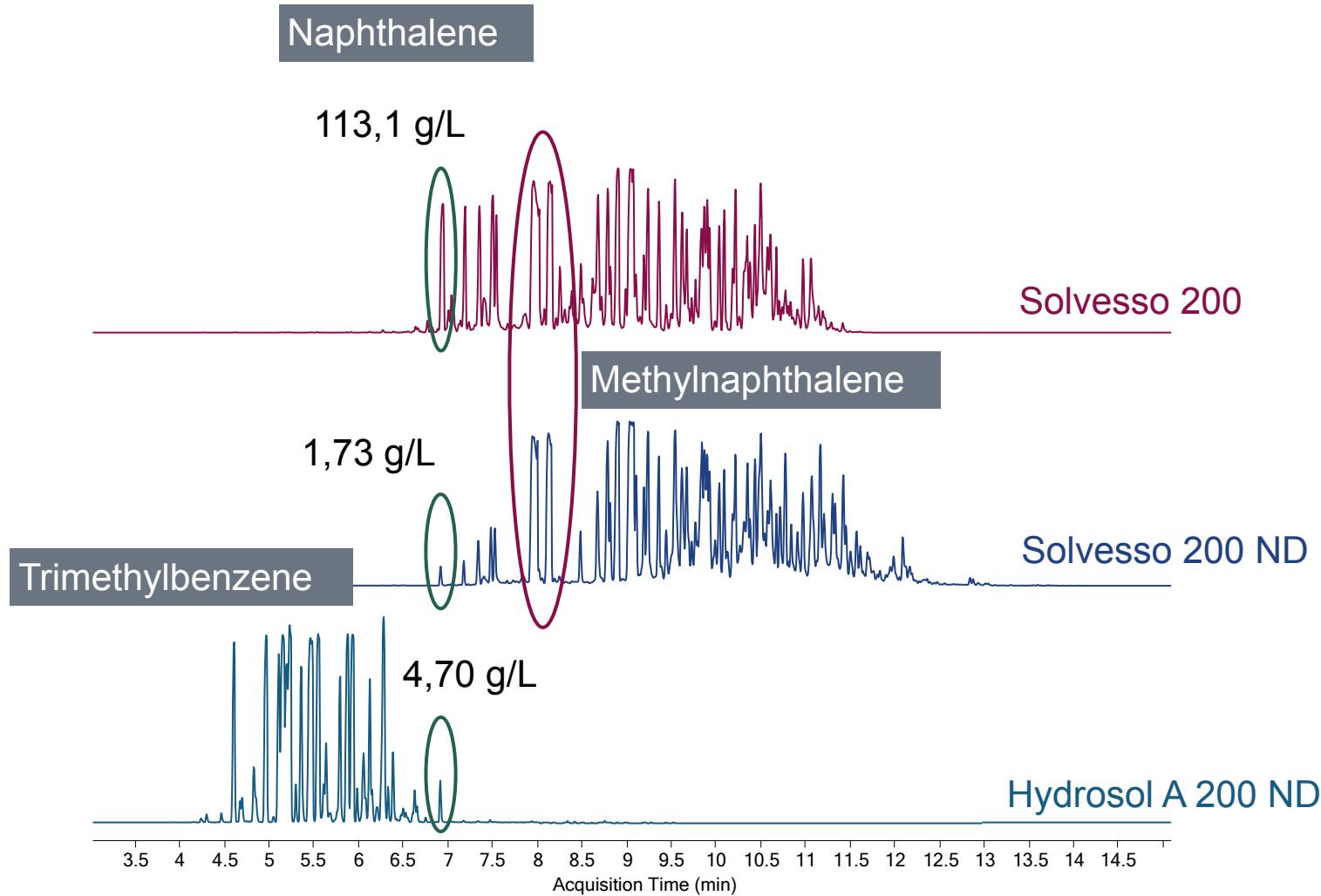
6,17 g/L



Solvesso 150 ND

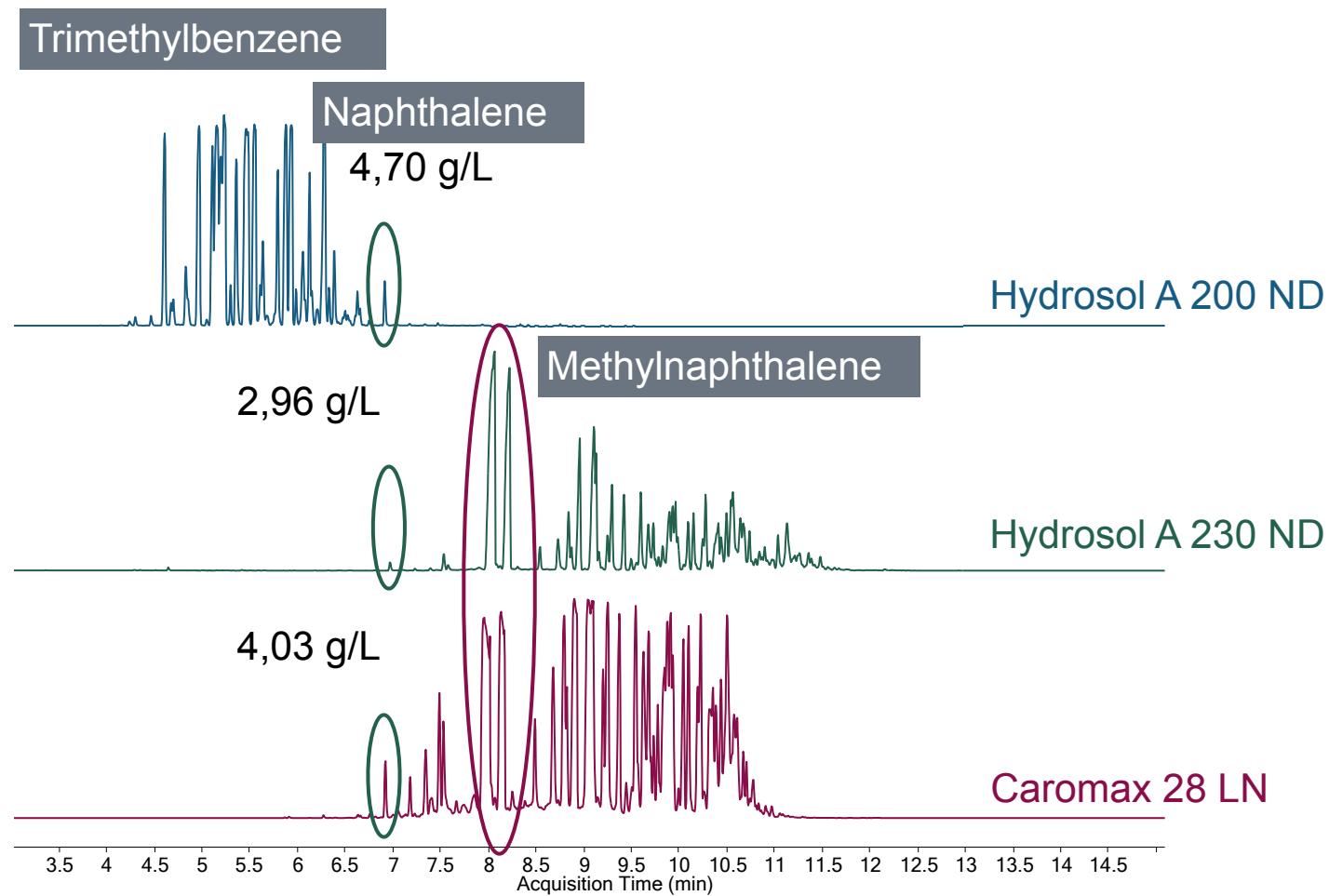
3.5 4 4.5 5 5.5 6 6.5 7 7.5 8 8.5 9 9.5 10 10.5 11 11.5 12 12.5 13 13.5 14 14.5
Acquisition Time (min)

Solvent naphtha co-formulants - 2014



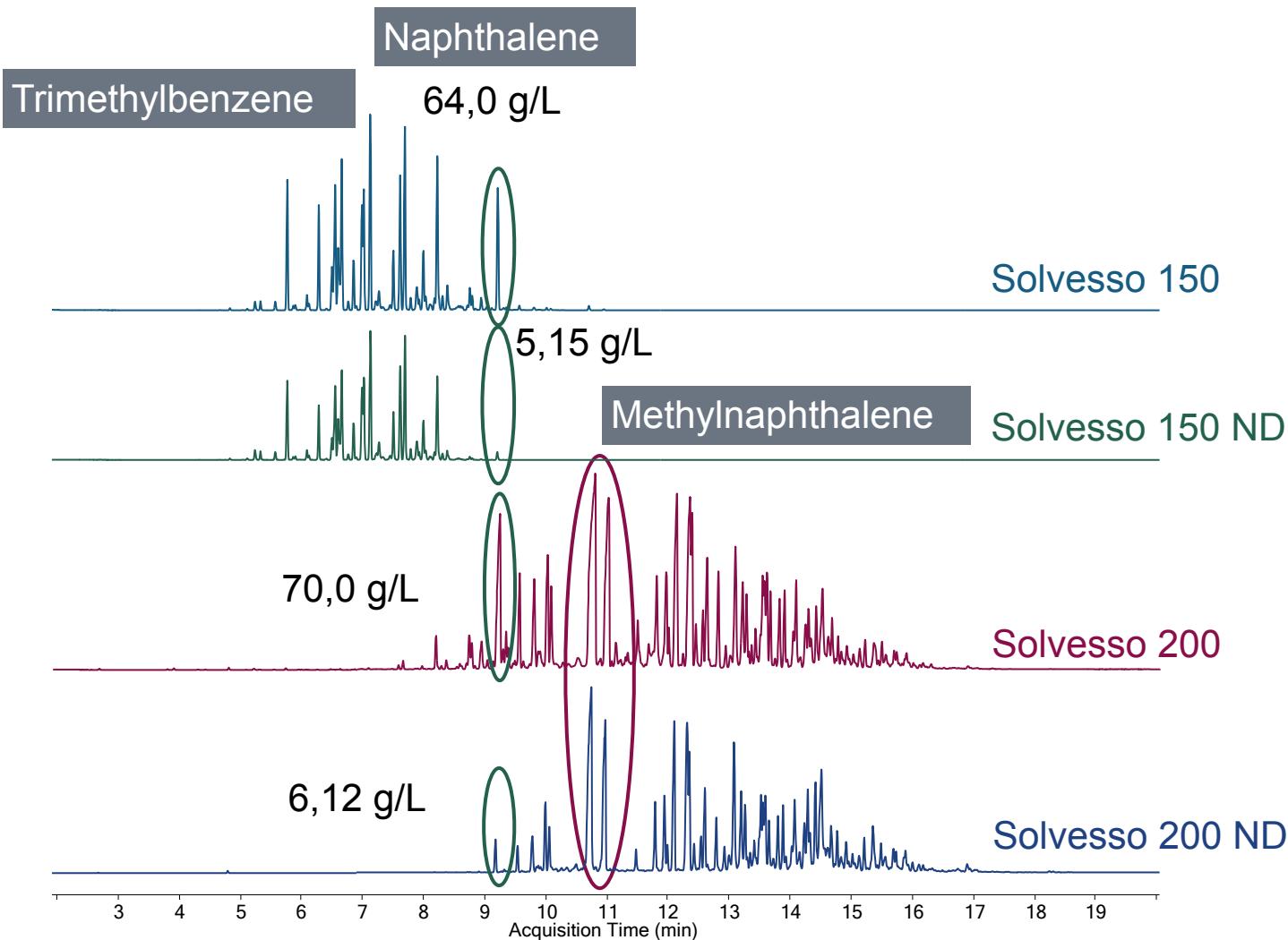


Solvent naphtha co-formulants - 2014

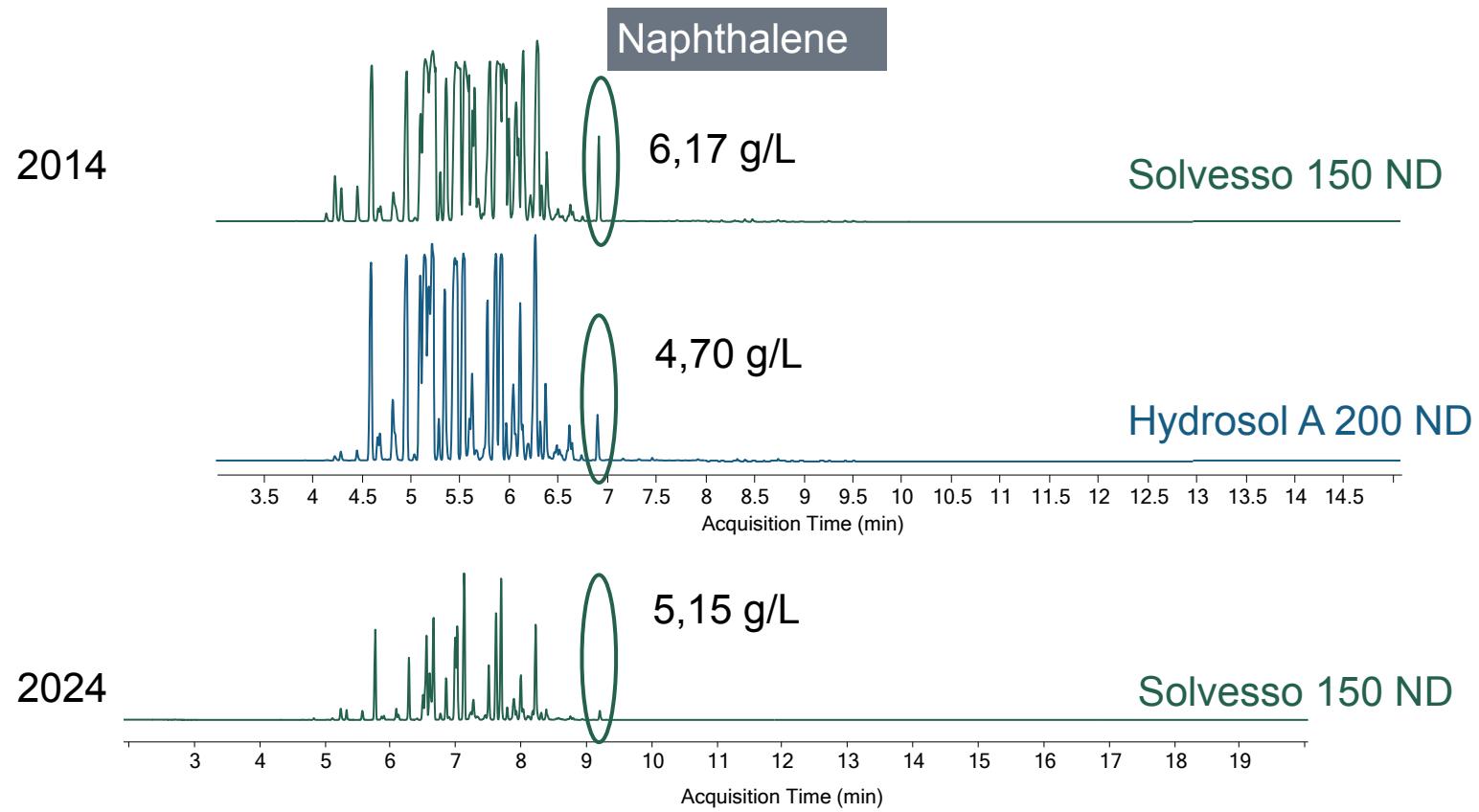




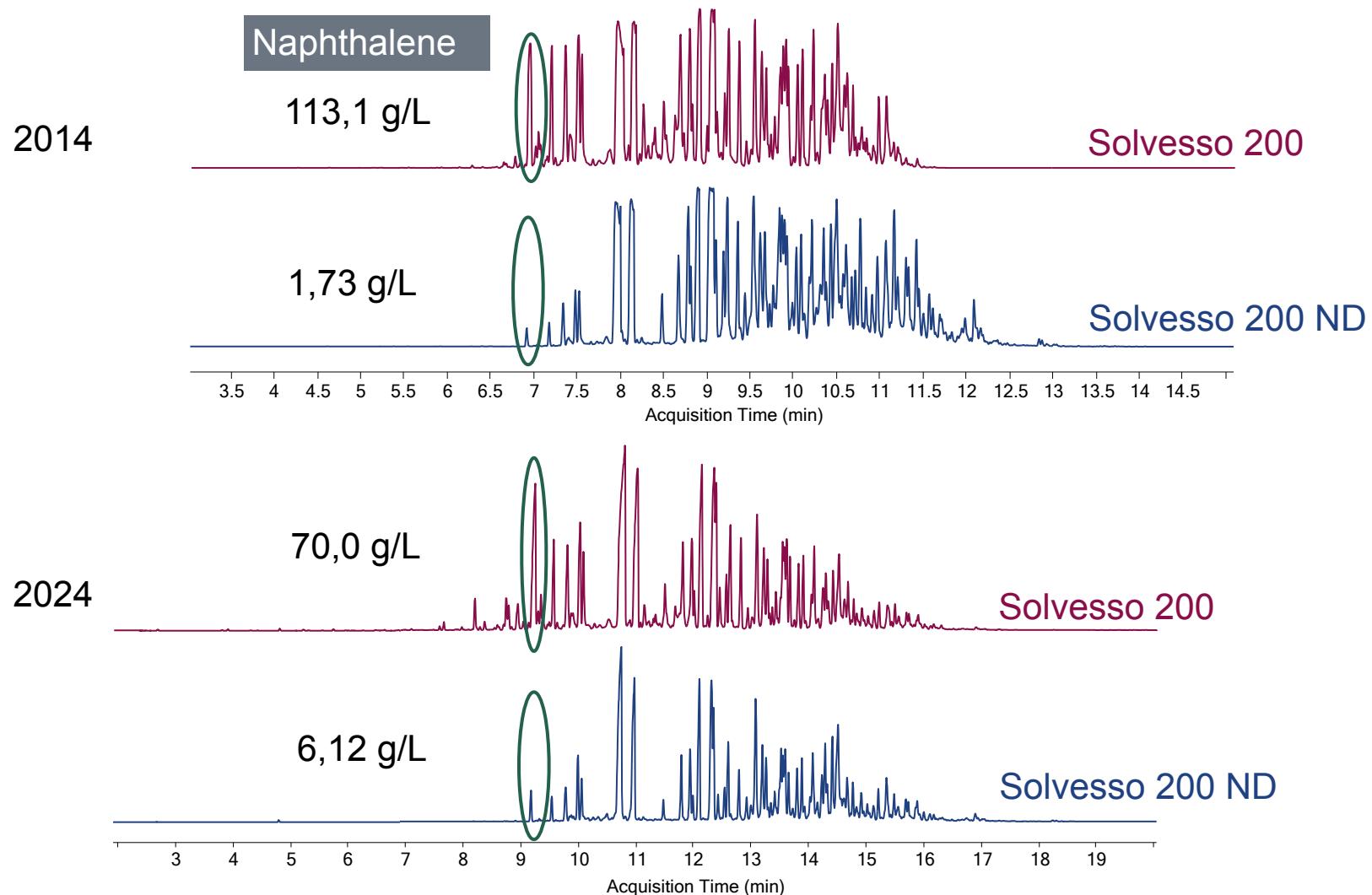
Solvent naphtha co-formulants - 2024



Solvent naphtha co-formulants - evolution



Solvent naphtha co-formulants - evolution





Solvent naphtha co-formulants - conclusion

- Requirements for co-formulants are growing over the years.
- Toxicological and/or ecotoxicological relevant co-formulant substances are not accepted anymore.
- In solvent naphtha co-formulants unwanted substances/impurities can be removed technical, e.g., by discarding fractions of concerned temperature.
- The composition of solvent naphtha co-formulants varies between the charges and over the time, but depending on the fraction differently intense.



Solvent naphtha co-formulants – future prospects

- Analysis of the 2024 solvent naphtha samples for cumene.
- To have an eye for further regulatory developments.
- Expand the capacities and method availabilities of control with respect to analyse unacceptable co-formulants.



Contact:

