CTCPA

SUPPORTING
TOMORROW'S FOOD MODEL

Mass spectrometry, an essential tool for the analysis of food contact material migrations

CONTACT :

Julien Terrasse
Chef de projets Emballages
CTCPA Bourg en Bresse

jterrasse@ctcpa.org

ITAI
INSTITUT TECHNIQUE AGRO-INDUSTRIEL

cti réseau
COMPÉTITIVITÉ TECHNOLOGIE INNOVATION

OVERVIEW

01/ Quick presentation of CTCPA

02/ Food contact material and migration into food – Definition and regulation

03/ Uses of mass spectrometry in Food Contact Material migration analysis

04/ Conclusion

01/ Centre Technique de la Conservation des Produits Agricoles - CTCPA

8 **sites in France**

Including **4 technological halls**,
3 **laboratories**,
1 **industrialization department**
1 **monitoring** and **documentation center**

90 **expert employees**

Engineers, doctors, technicians...

01/ OUR MISSIONS

CRÉDIT D'IMPÔT AGRÉMENT CIR RECHERCHE

CRÉDIT D'IMPÔT AGRÉMENT CII INNOVATION

02/ Food contact material: a few examples

- Different kind of polymers
  - Polyethylene
  - Polypropylene
  - Tritan® (Main monomers :Dimethyl Terephthalate & 1,4-Cyclohendimethanol)
  - Polyethylene Terephthalate
  - Polyamide
  - Polystyrene…

- Multilayer material
  - Tetra Pack®
  - Multiple layers of plastic films, cardboards, aluminium and adhesives

- Metallic cans
  - Coated with a thin layer of polymeric coating
  - Different technologies of polymerics resins

02/ Regulations

"Materials and articles, … , shall be manufactured in compliance with good manufacturing practice so that, under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could:

(a) endanger human health

(b) bring about an unacceptable change in the composition of the food

(c) bring about a deterioration in the organoleptic characteristics thereof"

REGULATION (EC) No 1935/2004 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

→ Specific regulations for the different types of packaging (e.g Commission regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food)

→ Restrictions on raw materials which could be used in formulation/resin synthesis – **List of authorised substances**

→ **Define SML (Specific Migration Limit)** = maximum levels for certain contaminants (e.g Commission regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs)

02/ Overall and specific migrations

Analysis in foodstuff are complexed (extraction, matrix effect,…) → Food simulants are defined in regulations for each kind of food (hydrophily, acidity, alcohol content, …)

List of food simulants

Food simulant	Abbreviation
Ethanol 10 % (v/v)	Food simulant A
Acetic acid 3 % (w/v)	Food simulant B
Ethanol 20 % (v/v)	Food simulant C
Ethanol 50 % (v/v)	Food simulant D1
Vegetable oil (*)	Food simulant D2
poly(2,6-diphenyl-p-phenylene oxide), particle size 60-80 mesh, pore size 200 nm	Food simulant E

Migration experiments are realised in those simulants within specific Time/ Temperature to mimic the storage/uses conditions of the packaging

Overall migration: gravimetric measure of all the substance which migrates from the packaging

Specific migration: Ensure that listed substances quantities are below their SML (from tenths of mg/kg to µg/kg)

02/ NIAS: Non-Intentionally Added Substances

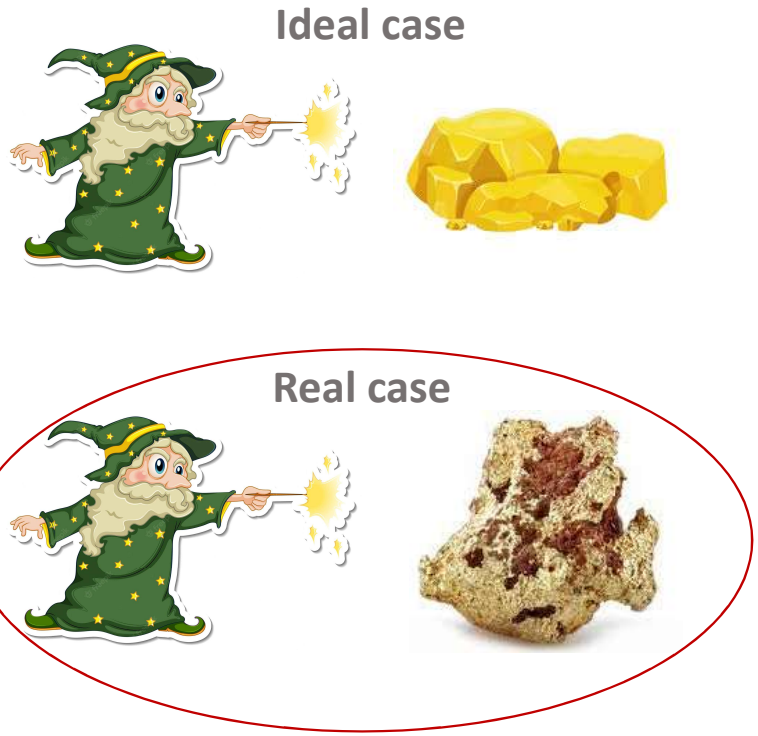
IAS: Intentionally Added substances (→ SML)

- Residual monomers
- Solvents
- Additives

NIAS : Non-Intentionally Added substances (→ ~~SML~~)

- Side reactions & decomposition products
- Oligomers & reaction intermediates
- Impurities & contaminants

Neoformed compounds: NIAS due to IAS reactions



If a substance is detected **above 10 µg/6dm²** (=kg food), then it is necessary to **identify them** (TSC33-NIAS Guidelines For Coated Rigid Metal Packaging Intended For Direct Food Contact)

03/ Why is mass spectrometry needed ?

Targeted screening (MS or MS/MS)

→ **Better LOD** than FID detector – specifically with SIM and MS/MS method

→ Direct **verification of identity** and potential coelution through MS spectrum

Untargeted screening (Orbitrap or TOF)

→ Identification without analytical standards thanks to exact mass and proposed molecular formula

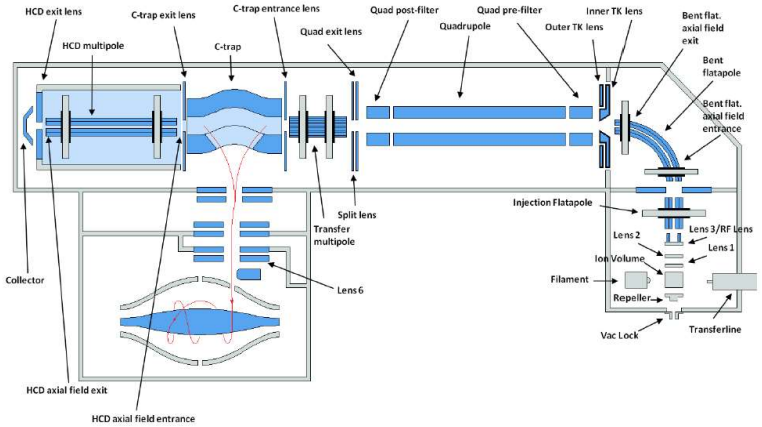
→ **Deconvolution software** to detect low intensity and coeluted peaks

→ Possibility to compare MS spectra with **homemade or/and international spectra database** (NIST, Wiley, …)

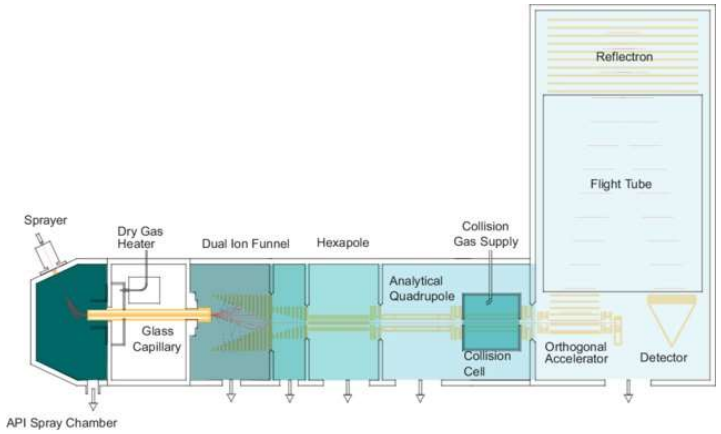
03/ Different analytical systems

Different analytical systems depending on the application

- Chromatographic methods: GC, HPLC
- Detectors: MS & MS/MS (simple or multi quadrupoles), HRMS (TOF, Orbitrap)
- Other technics: ICP-MS, Pyrolysis-GC-MS …



Orbitrap



Q-TOF

Mass precision < 5ppm → Access to exact mass

03/ Principal equipment used for FCM analysis

Volatile substances

HS-GC-(HR)MS
SPME-GC-(HR)MS

Residual solvent, volatile NIAS…

Semi-volatile substances

GC-(HR)MS

- Derivatisation
- Lower ionization energy

Residual solvents and monomers, oligomers of lower mass, …

Semi and non volatile substances

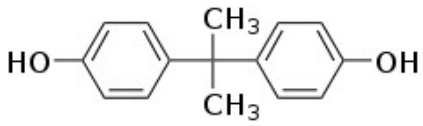
HPLC-(HR)MS
ESI or APCI ionisation

Monomers to high mass oligomers, …

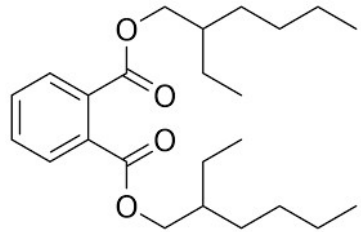
03/ Different applications carried out in CTCPA

Targeted screening in simulant or foodstuff:

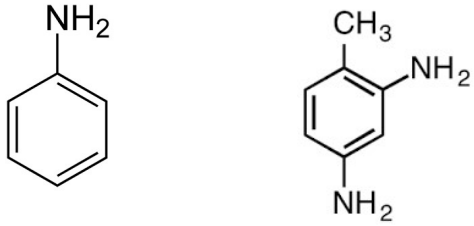
- Phthalates
- BPA and derivatives
- Primary aromatic amine
- Triethanolamine, …



BPA



DEHP



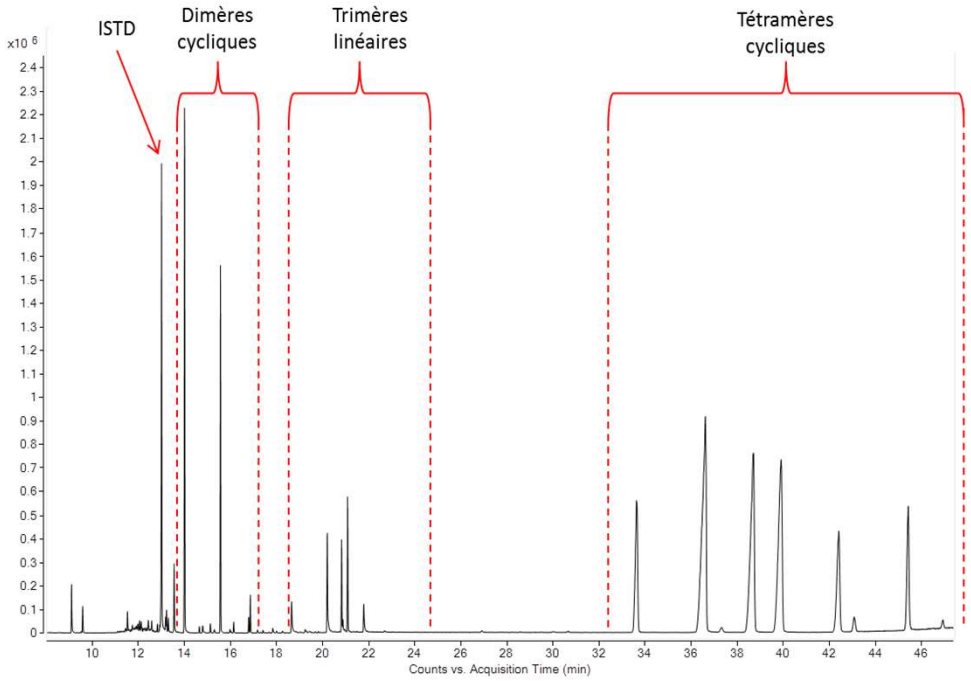
Aniline and 2,4-Diaminotoluène

Non-targeted screening:

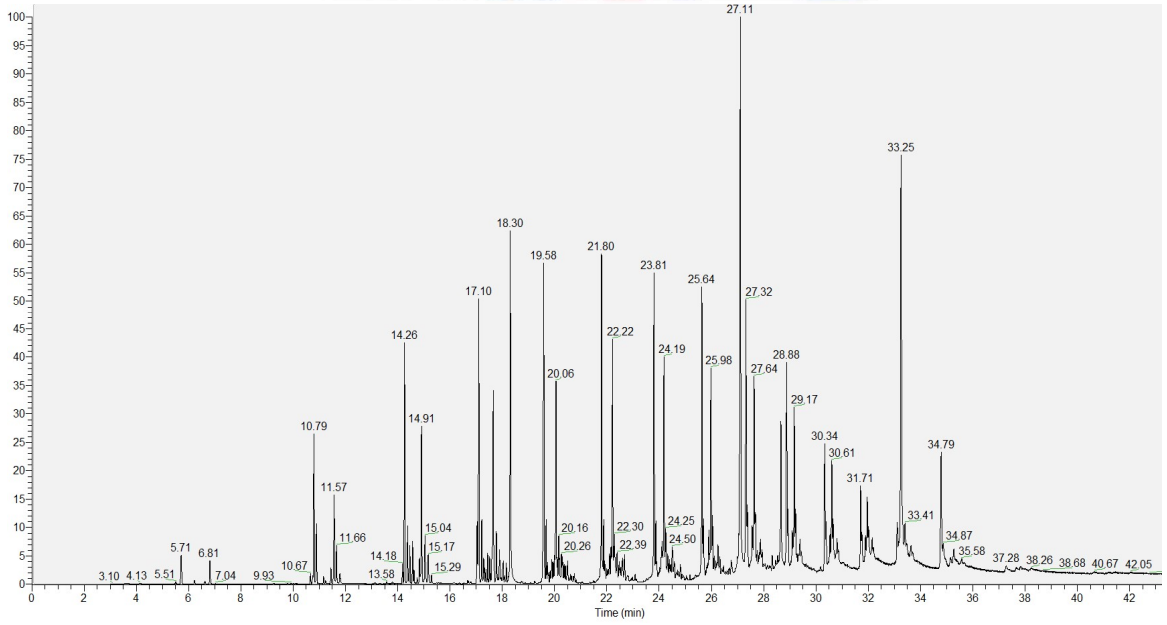
- **Usual NIAS screening** of FCM (e.g. Development of “cleaner” synthesis or formulation)
- Screening of NIAS/contaminants **along different processes** (slipping agents, degradation products through ageing and/or different conditions, ..)
- Aid to the **development of new process** in food packaging industry : **recyclability** for FCM production, **reuse** of FCM

03/ Different applications

Different packaging materials

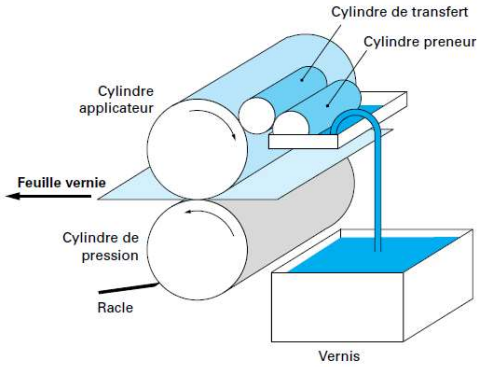


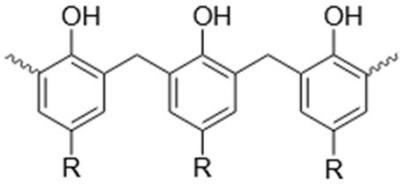
Polyester can coating extracted 24h @ 40°C in acetonitrile



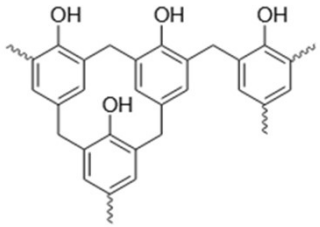
Polypropylene tray extracted 10 days @ 40°C in dichloromethane

03/ New NIAS identified in can coating using Tert-butylphenol-based phenolic resins

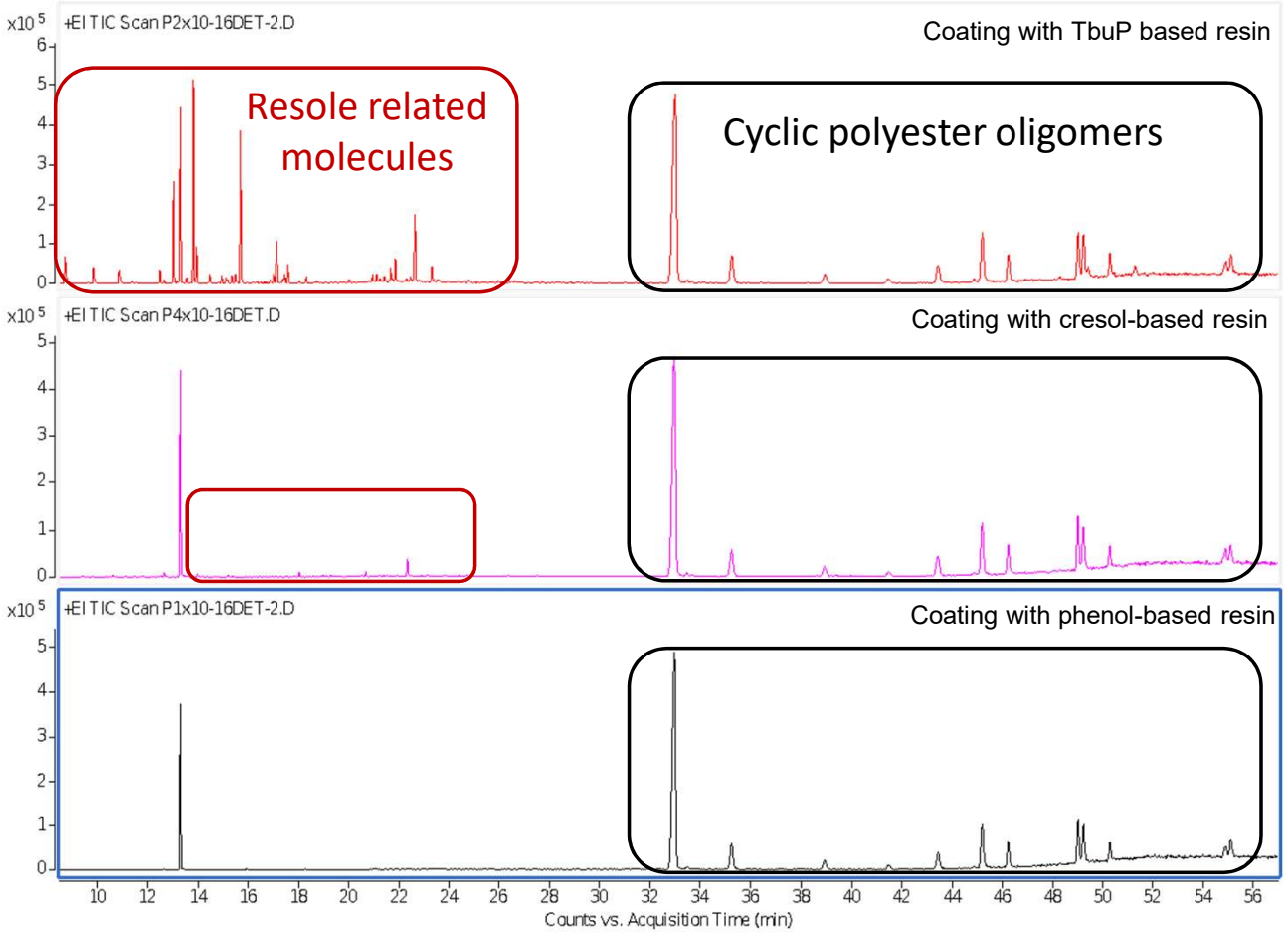




Alkylated-phenol based resole

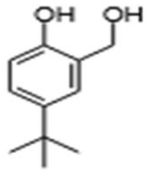


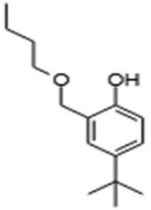
Phenol based resole



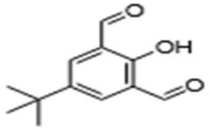
03/ New NIAS identified in can coating using Tert-butylphenol-based phenolic resins

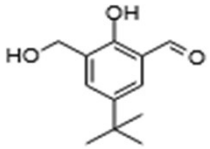
Known oligomers were identified: oligomers with unreacted methylol or butylated chains

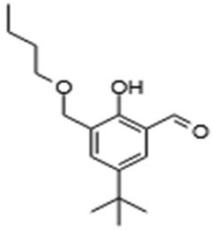


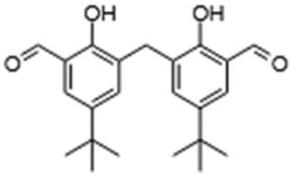


Aldehyde molecules were identified for the first time in a FCM, and directly found within TbuP resoles



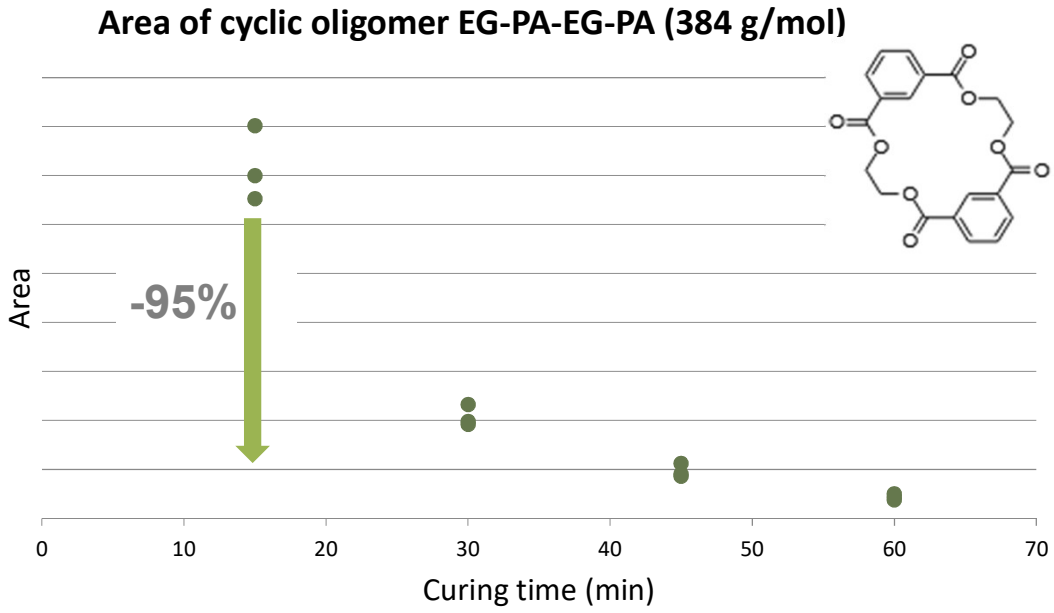


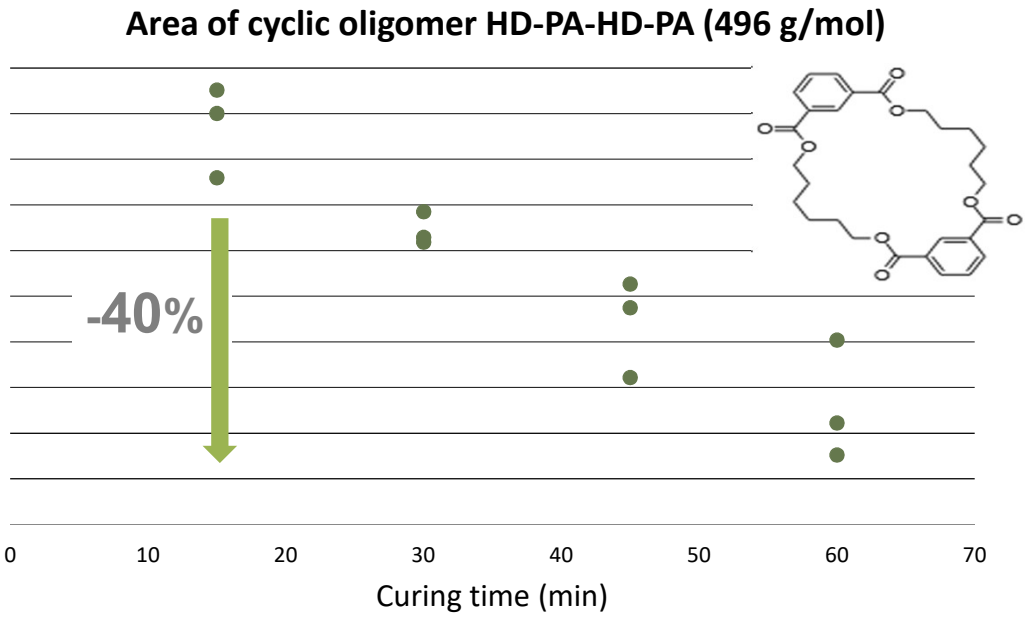




Terrasse, J., Martin, M., Dubail, S., Dole, P., Casabianca, H. Non-targeted screening of extracts from polyester-phenolic can coatings: Identification of new aldehyde molecules from resole-based resins. Talanta 243, 123351. https://doi.org/10.1016/j.talanta.2022.123351

03/ Influence of cure parameters on oligomer content in can coating



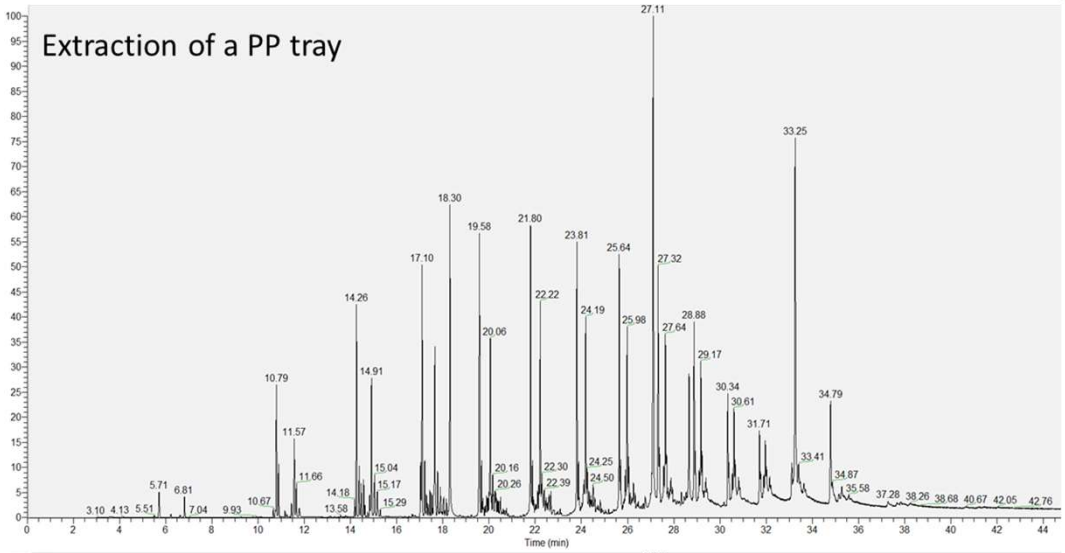


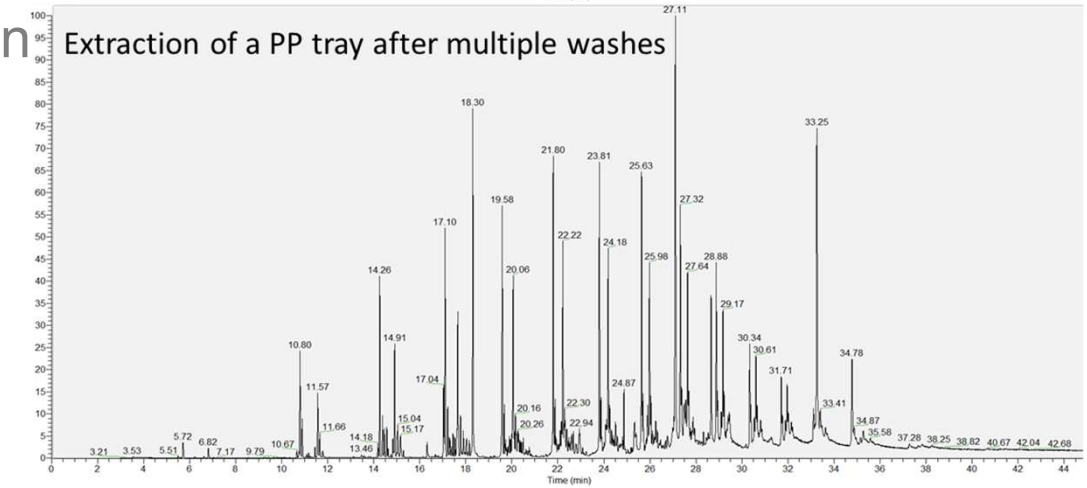
- Diminution of the overall content of cyclic oligomers with curing time
- Further analysis to determine which physical/chemical mechanisms led to these decrease

03/ Search of contaminants due to washing process

With the apparition of reusable packaging, as for example in fast food restaurants.

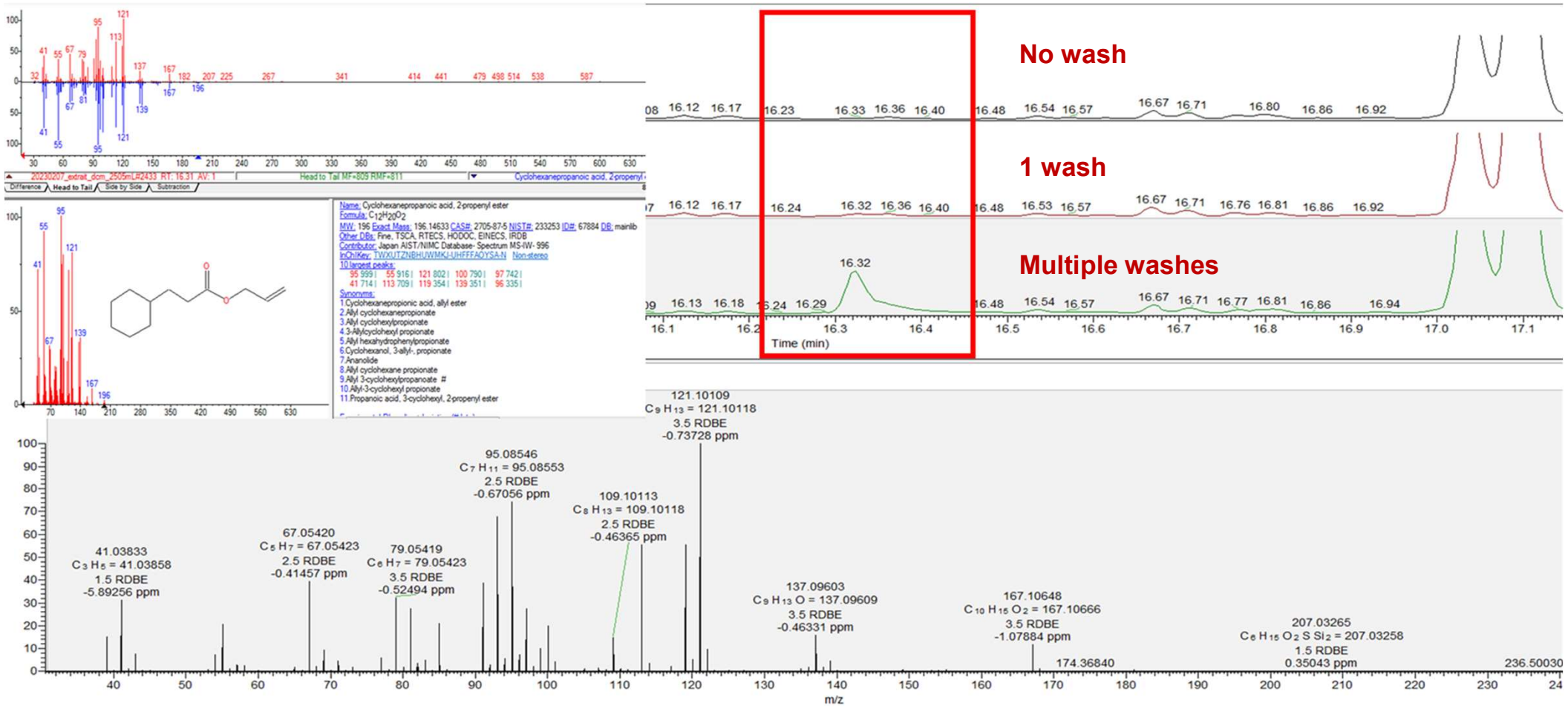
Is there a possible of contamination through the washing process ?





03/ Search of contaminants due to washing process

Contamination observed through the multiple washes – Detected after 1 wash thanks to deconvolution software



4/ Conclusion

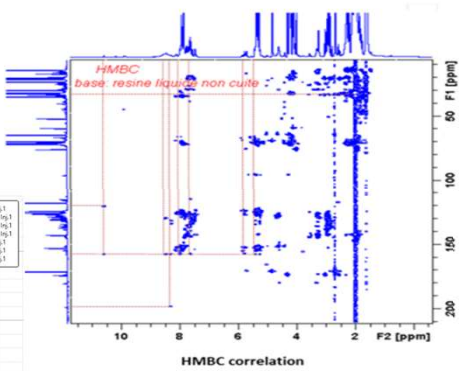
Mass spectrometry is an essential tool for the analysis of food contact material migration in order to:

- Detect and quantify substances in low concentrations (<10 µg/kg food)
- Identify unknown NIAS thanks to exact mass and proposed molecular formula
- Deconvolution software for data and statistical treatments

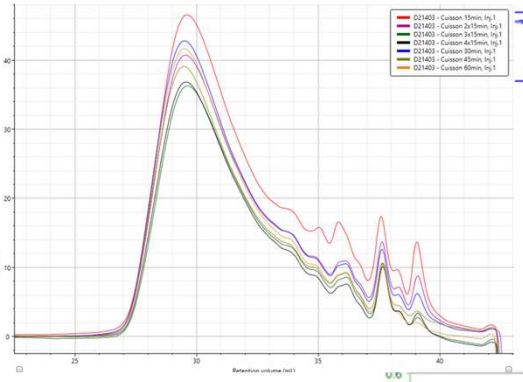
4/ Conclusion

But mass spectrometry results are not always sufficient to conclude on overall mechanisms:

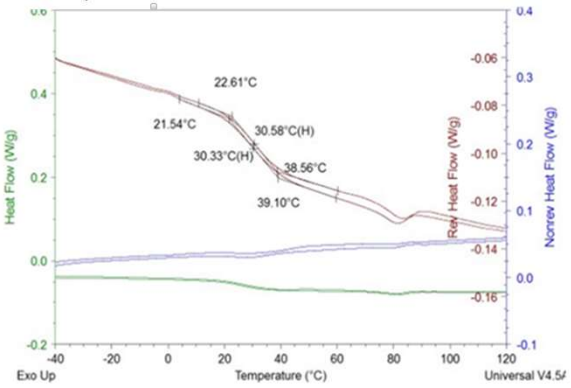
- Precise structure of NIAS (isomers)→ NMR



- Analysis of mass distribution → SEC analysis



- Analysis of glass transition → DSC



4/ Conclusion

Mass spectrometry will stay an essential tool in the future:

- Analytical systems are continuously improving through:
  - new sample introduction and ionisation: DART-MS, FIA, nano-ESI
  - new spectrometer: Ion Mobility Spectrometry

- Evolution of SML/TDI

(e.g. **Project** of BPA TDI reevaluation by EFSA – 4 **µg**/kg of body/day to 0,04 **ng**/kg of body/day)

- New problematic (conditions of uses, processes, …)
  - Recycling
  - Reuse
  - New FCM/contaminants

Thanks for your attention