Safety of cellulose-based materials for food contact

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FOREWORD

Cellulose-based materials: Paper and Board and films as FCM

- Applications where **intimate contact (primary packaging)** is involved, such as tea bags, baking papers, and filters, and direct contact packaging such as butter wrapping, sugar bags, and cartons for dry and frozen foods
- **Secondary packaging** (transport and distribution packaging).
- In **multilayer** (tetrabriks combined with plastics and Al, others)
- **Coated** paper
- **Films** of cellulose-based
- **Uncoated and untreated paper and board** is not suitable to pack food with very high moisture content
- The main application is contact with dry food.
- Completely different **manufacturing process** compared to plastics
- **Transparent films** cellulose-based

Paper and Board

- **(CoE (ReSAP 2005…) and BfR)**
- *Cooking Papers, Hot Filter Papers and Filter Layers: Recommendation XXXVI/1*
- Web link: http://bfr.zadi.de/kse/faces/resources/pdf/361-english.pdf
- *Paper and Paperboard for Baking Purposes: Recommendation XXXVI/2*
- Web link: http://bfr.zadi.de/kse/faces/resources/pdf/362-english.pdf
- *Absorber pads based on cellulosic fibres for food packaging: Recommendation XXXVI/3*
- Web link: http://bfr.zadi.de/kse/faces/resources/pdf/363-english.pdf

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Recycled Paper & Board

a) identify the source of any contaminants;

b) establish a methodology for reducing those contaminants to a safe level in the final product;

c) state any restrictions on food type which might result from a risk assessment of the above steps.

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Safety of Cellulose-based FCM

Assessment taking into account **the intended use** of the material including:

- food type,
- contact time
- temperature
- the likelihood of transfer of constituents during that use.

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Testing: extraction and migration

- Preparation of a cold water **extract**
- Preparation of a hot water **extract**
- Preparation of an organic solvent **extract**
- Conditions for determination of **migration** from paper and board using modified polyphenylene oxide (MPPO, Tenax) as simulant

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Testing: Target análisis (I)

- Determination of cadmium, lead and chromium in an aqueous extract
- Determination of mercury in an aqueous extract
- Determination of pentachlorophenol in an aqueous extract
- Determination of transfer of antimicrobic constituents (migration): (BIT (1,2-Benzisothiazolin-3-One), MIT (2-methyl-4-isothiazolin-3-one), CMIT,etc.)
- Primary aromatic amines (migration)
- Michler ketone (diethylaminobenzophenone, DEAB) (migration)

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Testing: Target análisis(II)

- Determination of the fastness of fluorescent whitened paper and board
- Polyaromatic Hydrocarbons (PAHs)
- Phthalates
- Benzophenone
- Bisphenol A in food simulants.
- Mineral oils (MOHs and MOAHs)

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What recycled P&B can contain

- Functional absorbents to reduce the migration
- Functional barriers (Al, varnishes, coatings, films, etc.)
- Recycled fibers (scraps aren't considered recycled fibers)

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Compliance

- Global migration limit: 10 mg/dm^2
- Absence of toxic substances and CMR
- Control of the substances with SML
- Identification and Quantification of NIAS
- Odour (<3)
- Absence of microorganisms (Regulation (EG) No. 852/2004)
- Biocides

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Substances of concern

- Mineral oils(MOSH y MOAH)
- Endocrine disruptors: Polifluoroderivatives (PFAS), surfactants, phthalates, bisphenol A and derivatives
- Plasticisers
- Metals
- Photoiniciators
- Primary aromatic amines (PAAs)
- Michler ketone (dimethylaminobenzophenone)

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How to demonstrate the compliance

TESTS

- Extraction in cold water
- Extraction in hot water
- In ethanol 95%
- In isoctane
- In 3% Hac (metals and PAAs)
- Migration to simulants for coated paper
- Migration to Tenax

- **Tests under the worst conditions of intended use**

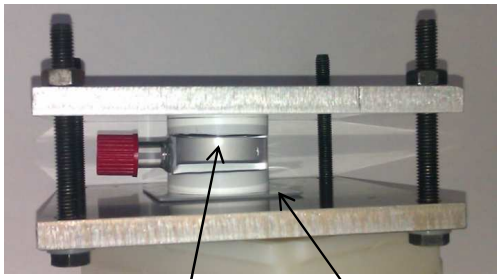
Indicators of recycled P&B:

- DiPN
- BPA

Results expressed as surface /mass of food:
13,3 dm^2/Kg for paper and board of 300 g/m^2

Migration tests, one layer contact

MIGRATION CELL



EU/10/2011

Simulant	Observation
A	Ethanol 10% (v/v) Hydrophilic character
B	Acetic acid 3% (w/v) Hydrophilic character: pH <4.5
C	Ethanol 20% (v/v) Hydrophilic character: alcohol content <20%, organic ingredients
D1	Ethanol 50% Lipophilic character: alcoholic food and emulsions
D2	Vegetable oil (ethanol 95%, isooctane): free fat at the surface Lipophilic character
E	Tenax ® (2,6-diphenyl-p-phenylene oxide) Dry foods

✓ **Time** and **temperature** conditions

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Practical details

- Take always a representative sample.
- Uncoated P&B are tested with Tenax
- Coated paper and board are tested with liquid simulants.
- Tenax rate in the test: 4 g/dm^2
- Clean Tenax before using.
- Using Tenax, OM is not applicable
- After the exposure Tenax has to be extracted and recovered
- Optimized extraction of Tenax is always required.

Referencias interesantes

An Overview of Approaches for Analysing NIAS from different FCMs
ILSI Europe Report Series , 05/04/2023
Oldring, Peter Sherwin Williams ; Faust, Birgit; Gude,Thomas; Lesueur, Céline; Simat, Thomas; Stoermer, Angela; Van Hoek, Els; Nerin, Cristina

Guidance in selecting analytical techniques for identification and quantification of non-intentionally added substances (NIAS) in food contact materials (FCMS)
Cristina Nerín [1], Siméon Bourdoux [2], Birgit Faust [3], Thomas Gude [4], Céline Lesueur [5], Thomas Simat [6], Angela Stoermer [7], Els Van Hoek [8], Peter Oldring [9]
Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 2022 Mar;39(3):620-643.
doi: 10.1080/19440049.2021.2012599. Epub 2022 Jan 26.

Methodologies to Assess the Biodegradability of Bio-Based Polymers—Current Knowledge and Existing Gaps
João Ricardo Afonso Pires, Victor Gomes Lauriano Souza, Pablo Fuciños, Lorenzo Pastrana and Ana Luísa Fernando
Polymers 2022,14,1359. https://doi.org/10.3390/polym14071359

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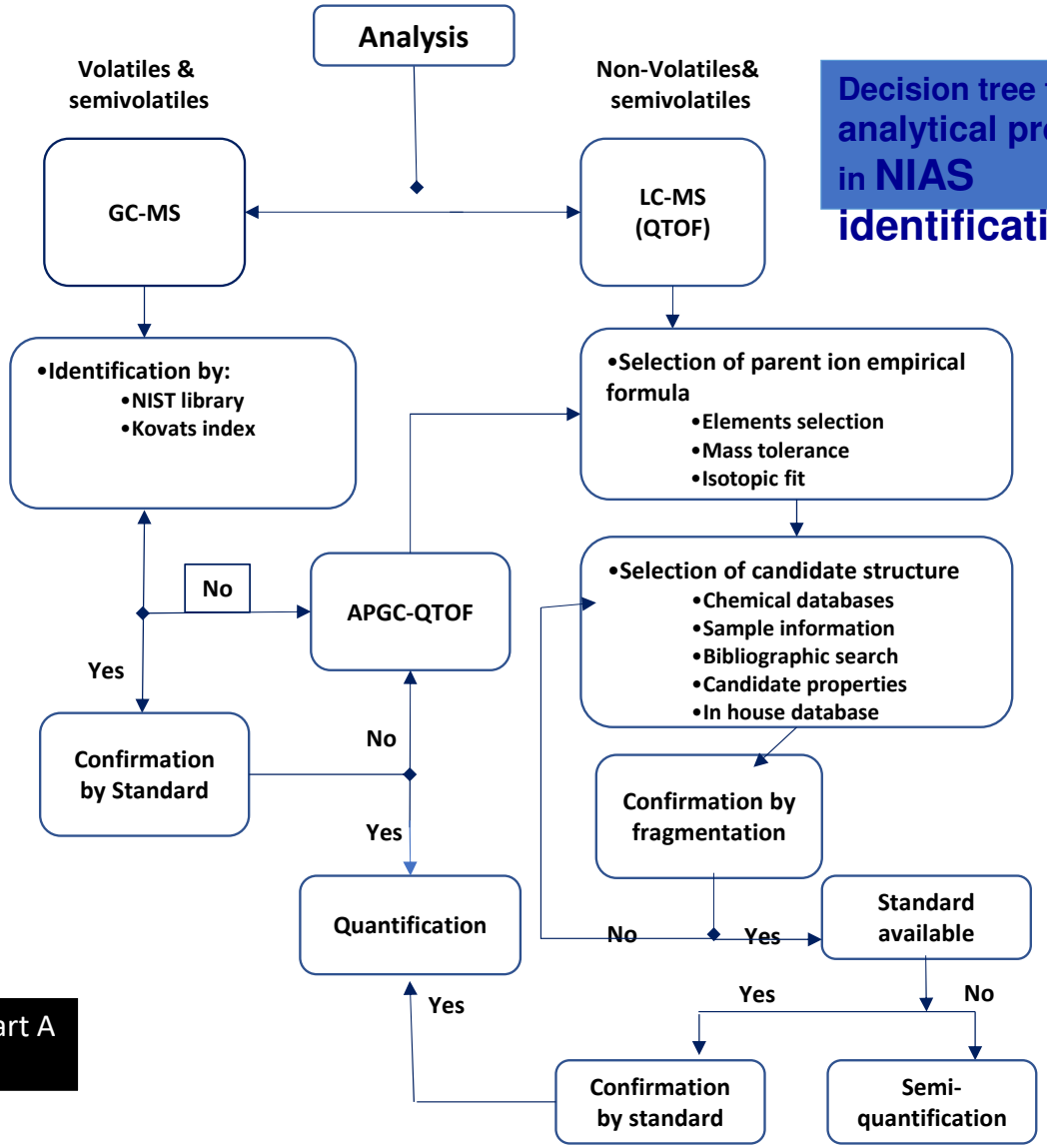
Decision tree for the analytical procedure in NIAS identification

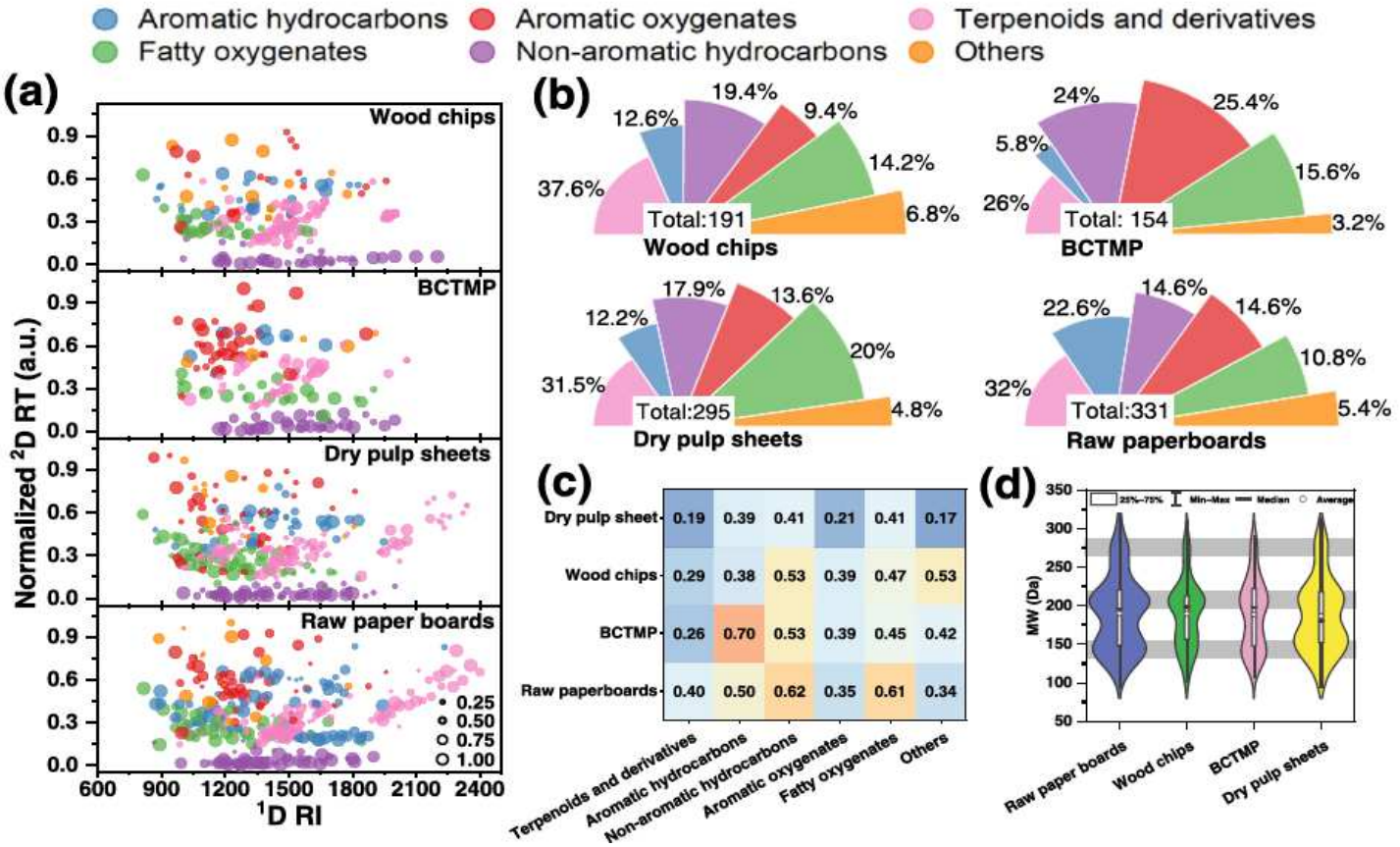
Sample preparation



C. Nerin*, P. Alfaro, M. Aznar, C. Domeño
Anal. Chim. Acta. Volume 775, 2 May 2013, Pages 14–24
DOI:10.1016/j.aca.2013.02.028. 2013

C Nerin et al. Food Additives & Contaminants: Part A
DOI: 10.1080/19440049.2021.2012599

Volatile compounds found



BCTMP= Bleach chemi-thermo-mechanical pulp

Origin:

- Natural/raw materials
- Pro
- processing aids
- Functional additives (IAS)
- Degradatin compounds

Hanke et al, Food Packaging and Shelf Life 37 (2023) 101062

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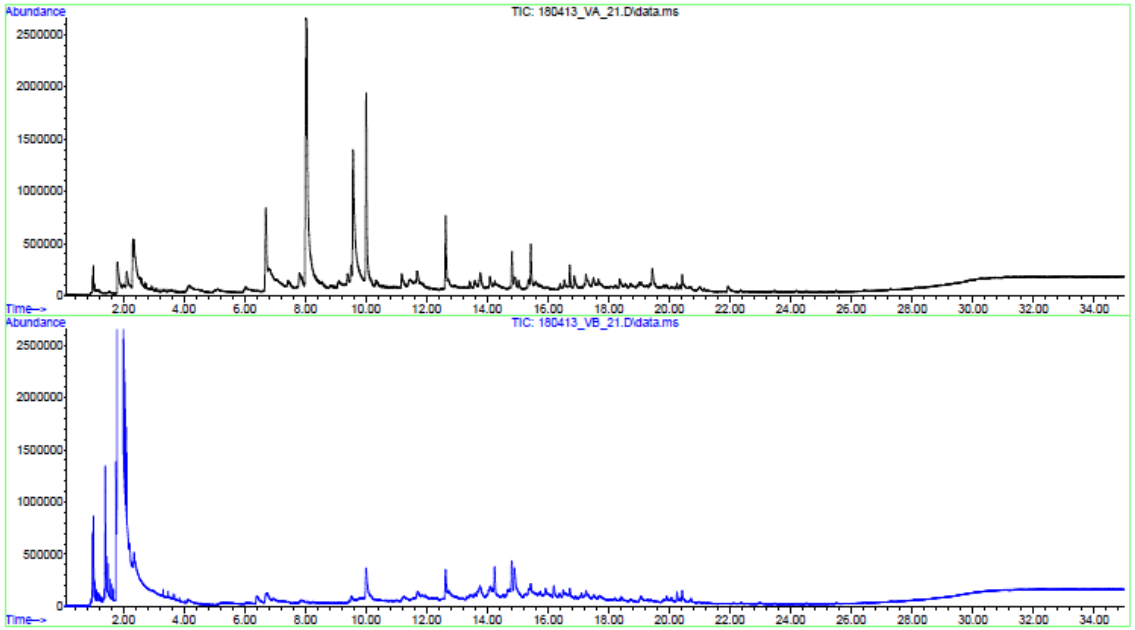
Migration from paper cups from coffee machines

2 h/70ºC

Esther Asensio, Teresa Peiro and Cristina Nerín
Determination the set-off migration of ink in cardboard-cups used in coffee vending machines
Food and Chemical Toxicology, ***2019****, 130, 61-67;*
DOI:10.1016/j.fct.2019.05.022



Sample A

Sample B

HS-SPME-GC-MS (DVB/CAR/PDMS) con columna capilar HP-5MS

Migration from 0.48 ug/Kg para 3,5-di-tert-butyl-4-hydroxybenzaldehyde[b,d] in **simulant C** to 1942.5 ± 414.9 ug/Kg for ATBC en **simulant D1**

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Instrumental Olfactometry GC-O-MS

MS detector

Sniffing port

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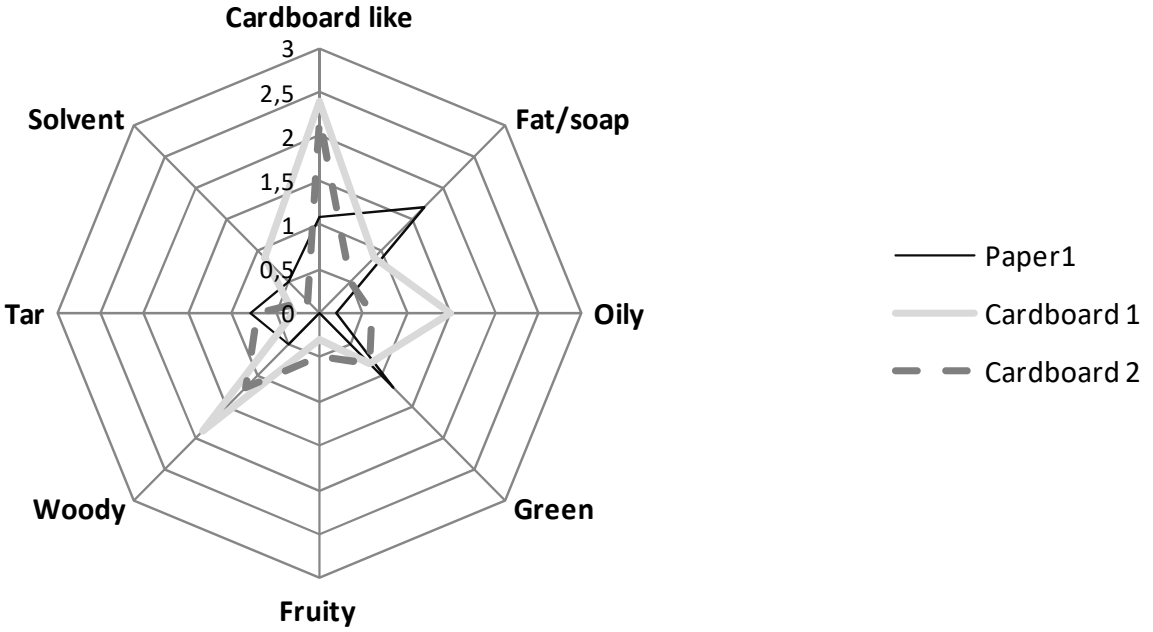
Compounds responsable for the odour by GC-O-MS

N°	Odorous compounds	IK	Odor	Material detected	FM
1	Toluene	1046	Paint	Paper1 PP4 Cardboard 1	55 48 60
2	Hexanal	1087	Fat, grass	Paper 1 Cardboard 1	82 72
3	b-Pinene	1116	Resin	Cardboard 1	45
7	Limonene	1203	Pine	Paper 1 Cardboard 1 Cardboard 2	55 70 74
8	1,2,4-trimethyl benzene	1276	Plastic, sweet	Cardboard 1	48
9	Octanal	1280	Fat, soap	PP4 PE1	90 75
10	1,3,5-trimethyl benzene	1290	Oily, aromatic	Paper 1 Cardboard 1 Cardboard 2	45 60 52
11	Cyclohexanone	1308	Mint and acetone odor	Paper 1 Cardboard 1 Cardboard 2	55 65 63
12	1,2,3-trimethyl benzene	1337	Oily,aromatic	Cardboard 1	67
15	Nonanal	1395	Fat, citrus, green	Paper 1 PP4 PE1 Cardboard 1 Cardboard 2	85 90 92 72 78
20	2-ethyl-1-hexanol	1485	Green	PP1 PP2 PP3 Paper 1 Cardboard 1 Cardboard 2	65 50 55 62 43 47
21	Longyfolene	1510	Woody	Cardboard 1 Cardboard 2	72 69
23	Benzaldehyde	1542	Fruity, sweet, almond cherry	PP1 PP2 Paper 1 PP3 PE2 Cardboard 1 Cardboard 2	45 58 57 52 49 42 61
30	Acetophenone	1671	Almond, flower	PP1 PP4 PE1 PE2 Paper 1 Cardboard 1 Cardboard 2	55 58 45 45 61 66 54
31	4-ethyl-benzaldehyde	1722	Fruity	PP4	43
32	Verbenone	1733	Spicy odor and camphoraceous	Cardboard 1	57
33	Naphthalene	1770	Tar	PP1 PP4 Paper1 Cardboard 1 Cardboard 2	66 49 52 61 55



Paula Vera, Elena Canellas and Cristina Nerín. Compounds responsible for off-odors in several samples composed by polypropylene, polyethylene, paper and cardboard used as food packaging materials
Food Chemistry, ***2020,*** *309, 125792, DOI:10.1016/j.foodchem.2019.125792*

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Migration of surfynol from printed board

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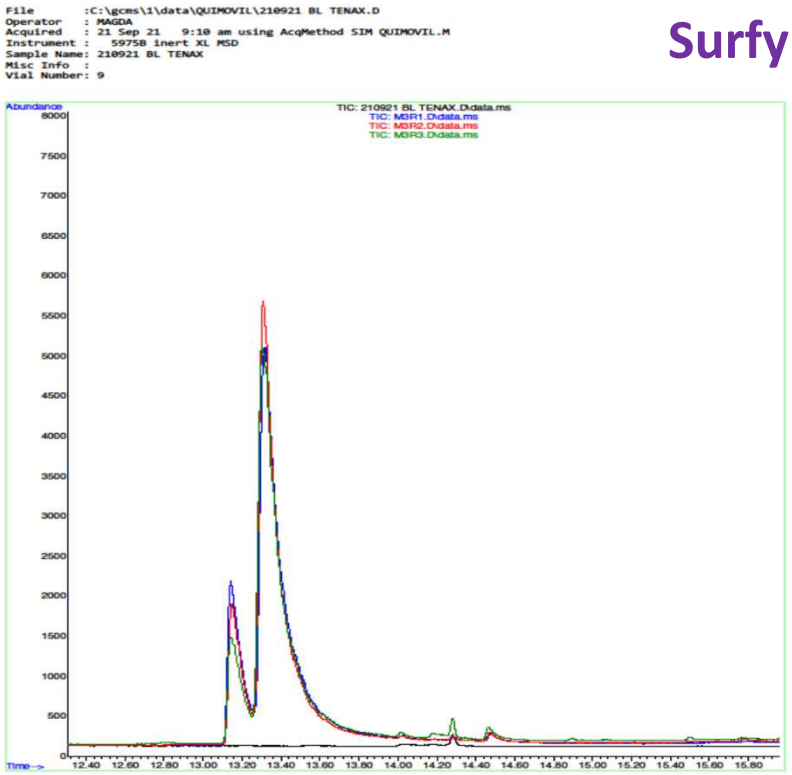


UPLC –qTOF-MS

Surfynol: 2,4,7,9-tetrametil-5-decino-4,7-diol (CAS 126-86-3)

Simulant	M1	M3	M5
Tenax	447± 8 µg/dm^2	377 ± 7 µg/dm^2*	370 ± 7 µg/dm^2
Simulant	**M1**	**M3**	**M5**
Tenax	2.68± 0.7 mg/Kg	2.26 ± 0.5 mg/Kg*	2.22± 0.5 mg/Kg*

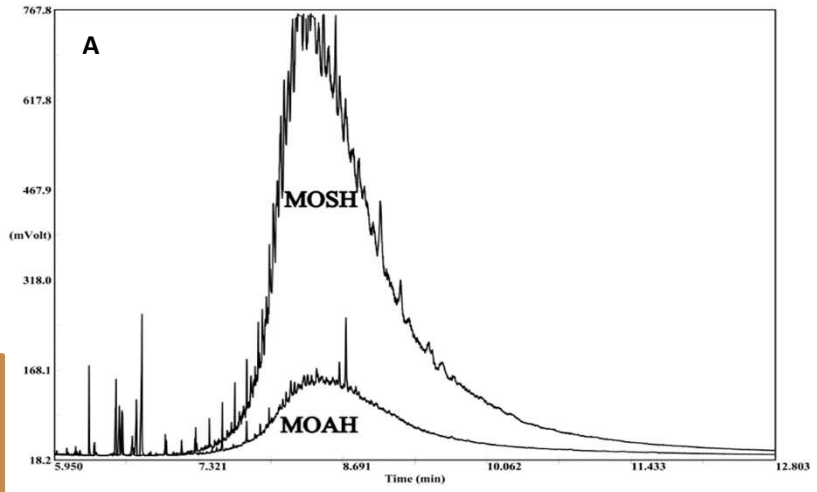
LOD 15 µg/Kg, ppb **SML = 50 µg/Kg**

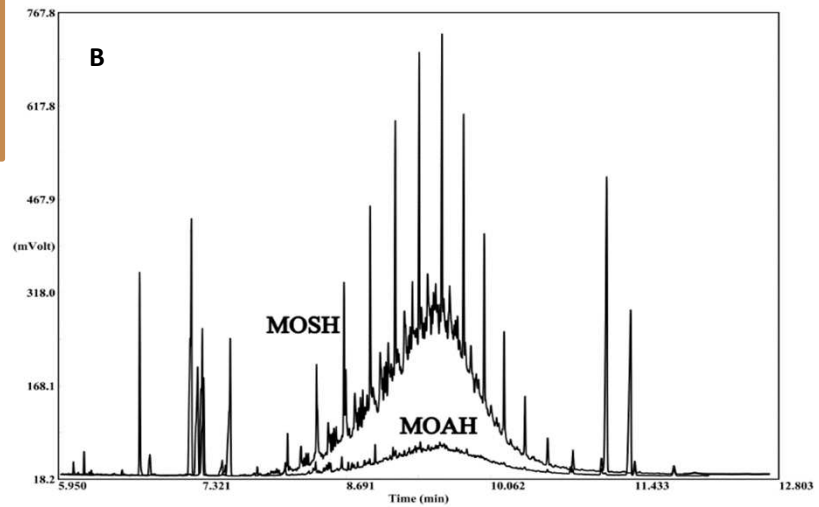
Nerin et al *Food and Chemical Toxicology 113 (2018) 115–124*
https://doi.org/10.1016/j.fct.2018.01.044

García Calvo et al. Food and Chemical Toxicology 146 (2020) 111849
https://doi.org/10.1016/j.fct.2020.111849

Mineral oils

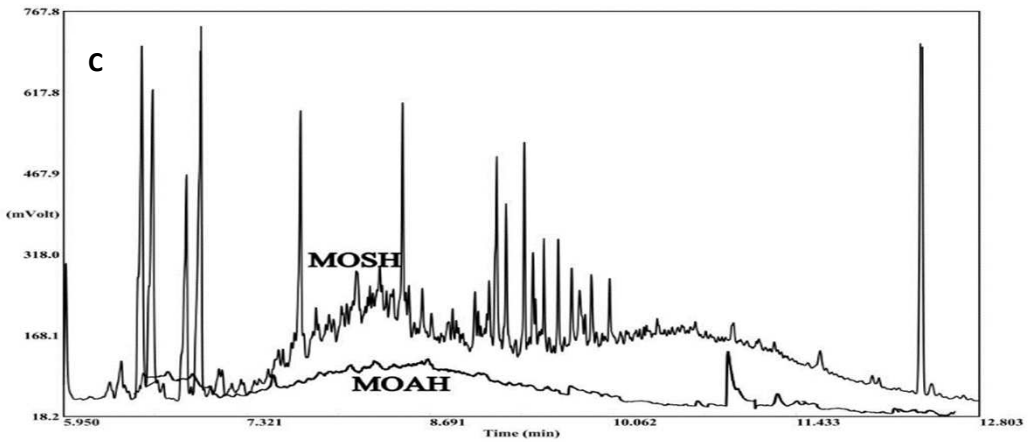
GC-FID





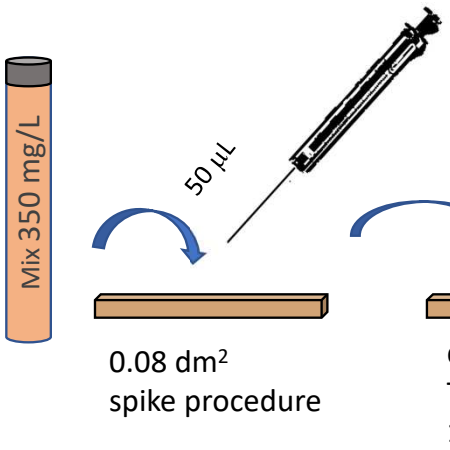
Sample	n-alcanre range	MOAH concentration
Mineral oil (A)	C13-C35	-----
rPet (B)	C14-C25	8,62 y 16,33 mg kg^{-1}
Recycled board (C)	C14-C28	25,12 mg kg^{-1}

RSD > 10%.

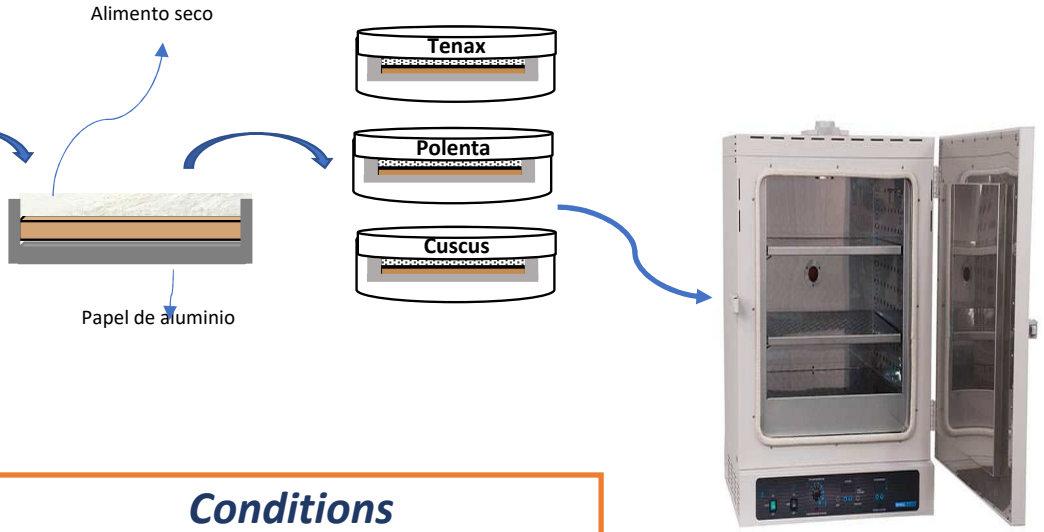


Migration of MOAHs from board

Spiking the board



Migration test



Regulation EU/10/2011

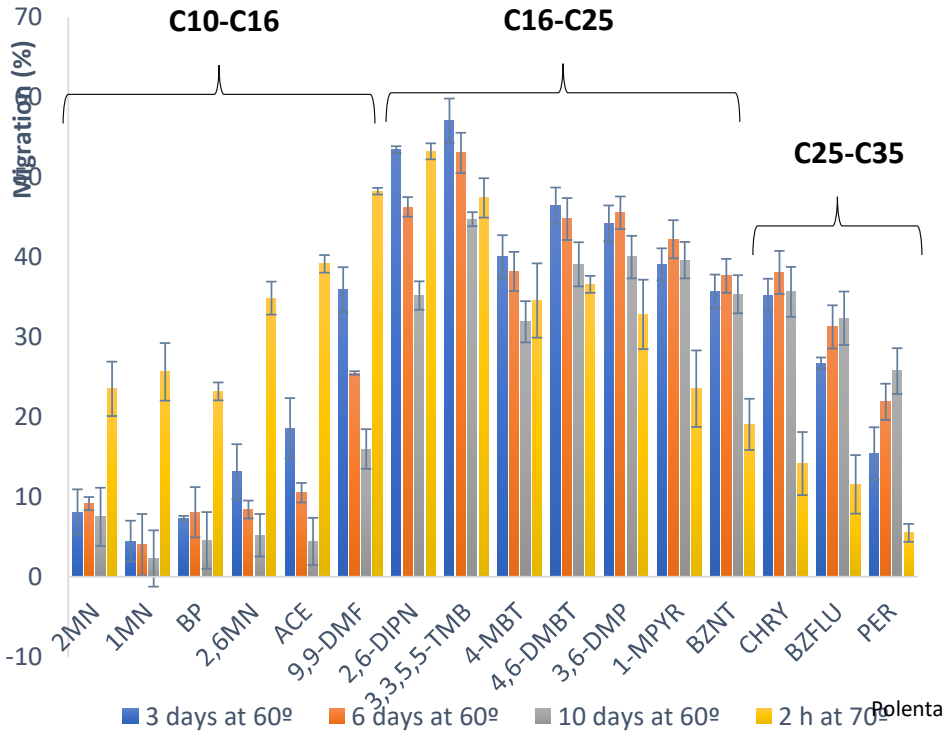
Norm UNE-EN 14338

Conditions

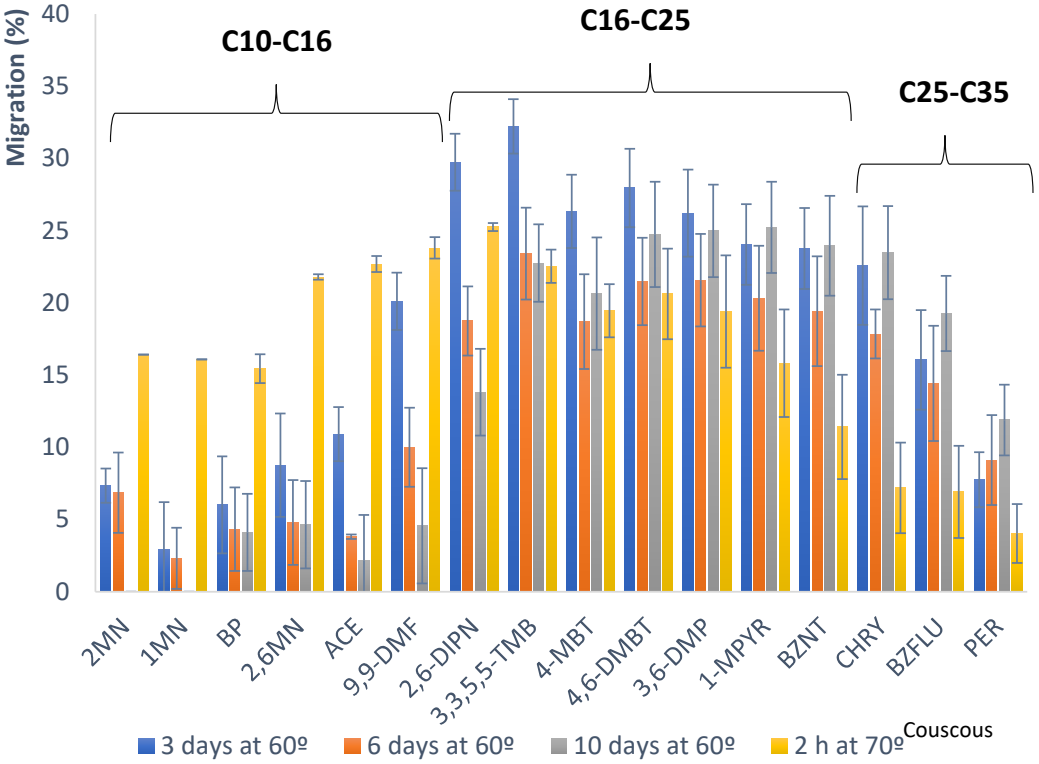
- ***2 h a 70 ºC (hot food)***
- ***10 days a 60 ºC (storage)***
- ***3, 6 y 10 days a 60ºC***

Mineral oils

Migración Polenta



Migración Cuscús



- **C10-C16: (polenta <40%, Cuscús < 25%)**
- **C16-C25: (polenta <60%, Cuscús < 35%)**
- **C25-C35: lenta y más baja**

Análisis del cartón después de la migración

- **0% no hubo retención de los analitos**
- **100% todos los analitos se retuvieron**

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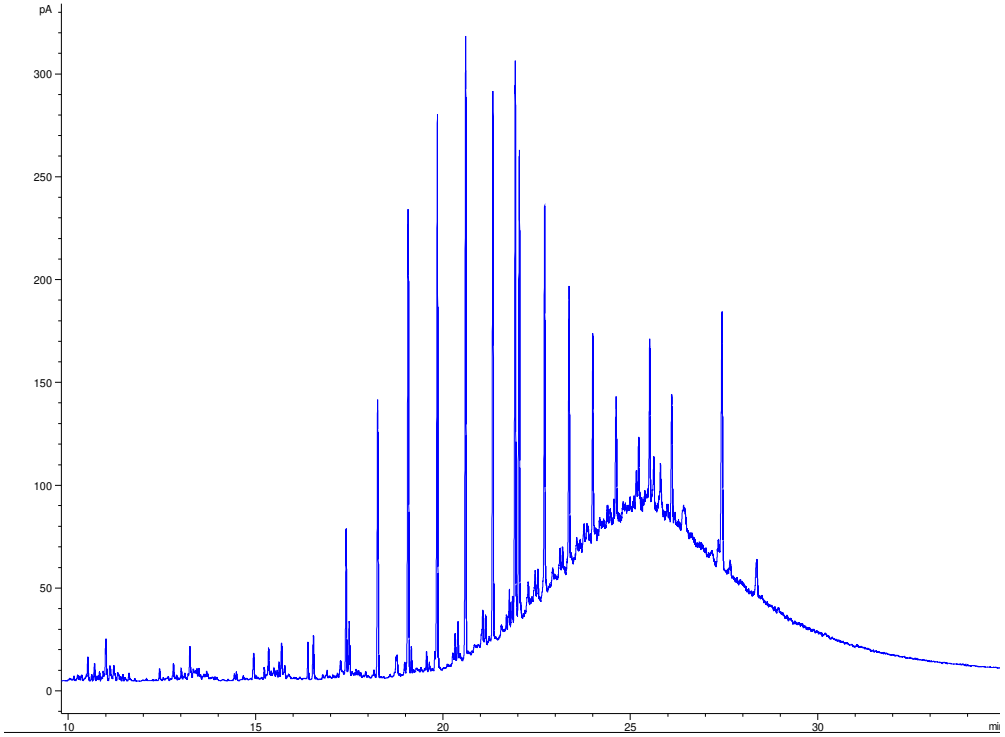
Migration of paraffin from coated board

GC-FID



Results

Migration to Tenax	Limit (SML) according to Swiss Regulation
170 ± 17 µg/dm2	(50 ng/dm^2)

Approach to solve the problem of identification

Use the specific databases for FCM

CPPdb (chemicals associated to plastic packaging) from Groh et al. DOI: 10.1016/j.scitotenv.2018.10.015

FCCdb (food contact chemicals database) from Groh et al. https://doi.org/10.5281/zenodo.3240108.

9391 compounds in total

BUT:
They need the analytical data (MS fragments, Retention Time, Ion mobility (CCS)

Identification using LIBRARIES

In-House library (UNIZAR) in UPLC-IMS-QTOF

Using certified/pure standards in our lab. Experimental CCS values

+

Prediction models for Retention time and CCS (developed in UNIZAR)

Mol file + **RT** + **CCS**

CPPdb (chemicals associated to plastic packaging) from Groh et al. DOI: 10.1016/j.scitotenv.2018.10.015

FCCdb (food contact chemicals database) from Groh et al. https://doi.org/10.5281/zenodo.3240108.

> 10,000 compounds with CCS and RT in the library

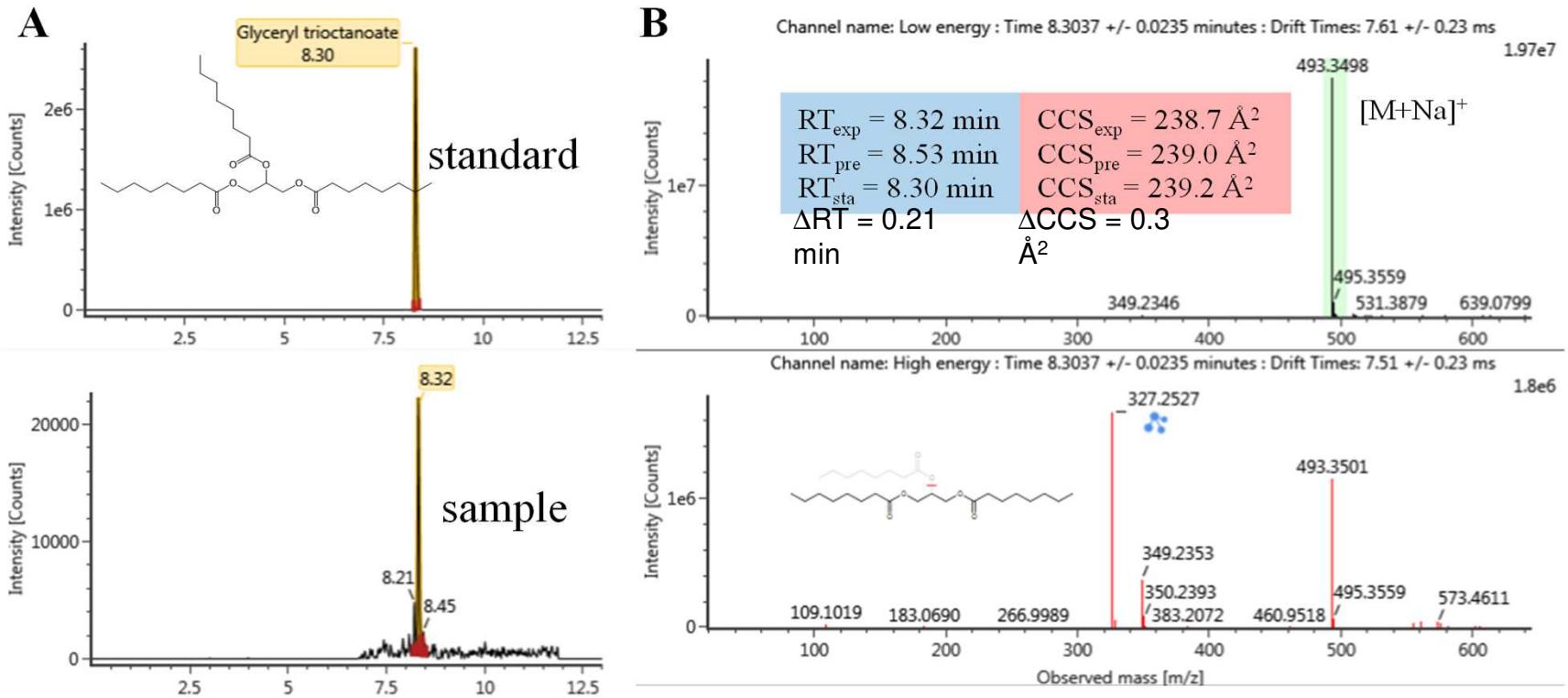
Song et al. J. Agric. Food Chem. 2022, 70, 9499–9508

In-House library (UNIZAR) in UPLC-QTOF-MS

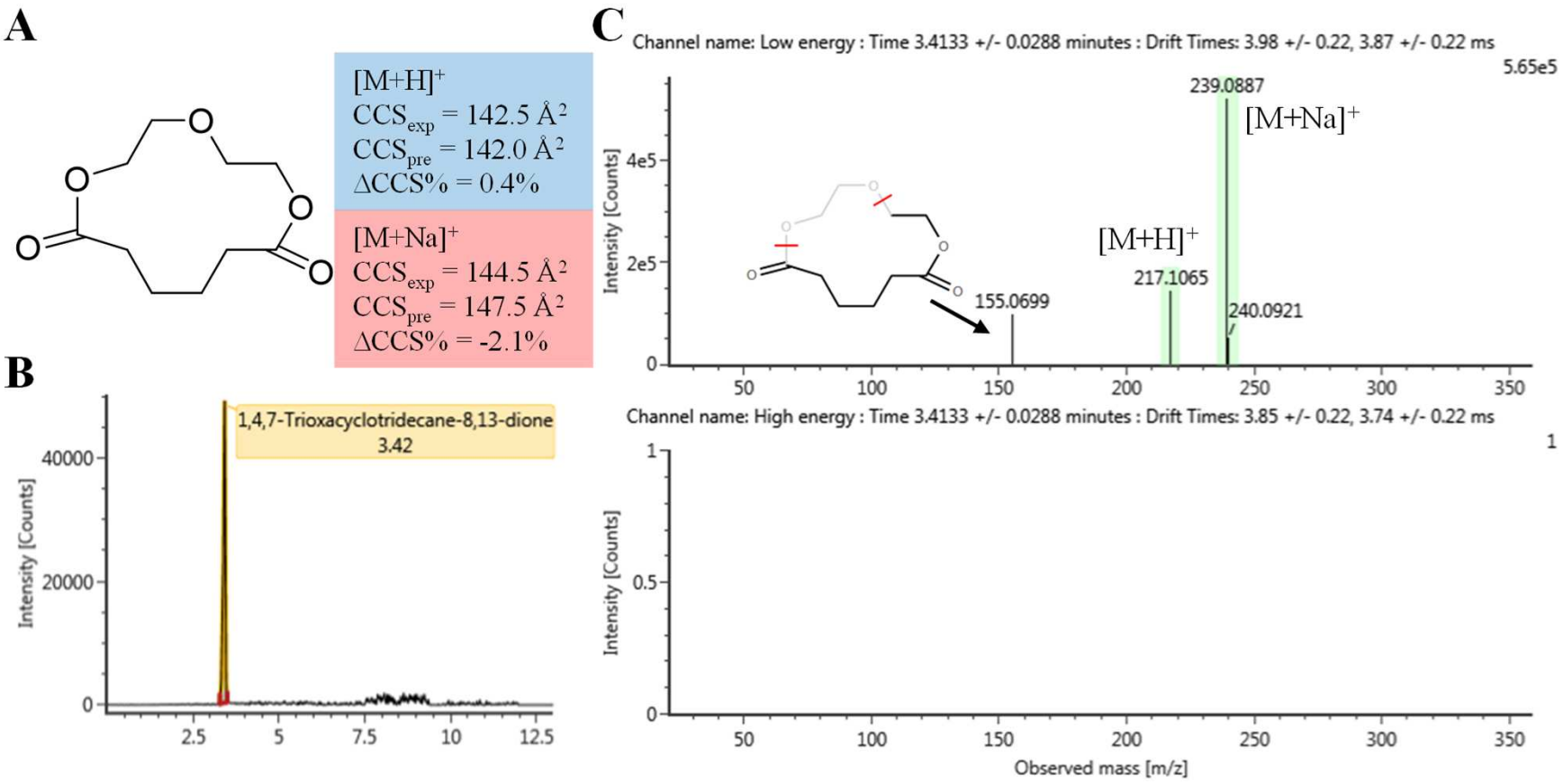
In-house MS/MS library and *mspcompiler* R package which contains 449 and 172 food packaging associated chemicals in positive and negative mode has been built. It Will be in public domain and available in https://zenodo.org/record/4454648

Su et al. Anal. Chem., 2023

Predicted RT and CCS improve the confidence of identification



CCS helps the identification of unknowns



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RISK ASSESSMENT OF NIAS

EUROPEAN LEGISLATION (EU/10/2011)

NATIONAL LEGISLATION

TOXICITY REPORTS

NO TOXICITY DATA

↓

Threshold of Toxicological Concern (TTC) approach
(not suitable for carcinogenic, mutagenic or teratogenic compounds)

↓

CRAMER RULES

Threshold of Toxicological Concern (TTC)

TOXICITY CLASIFICATION-Cramer rules (Toxtree v1.51)

Class I (Low)

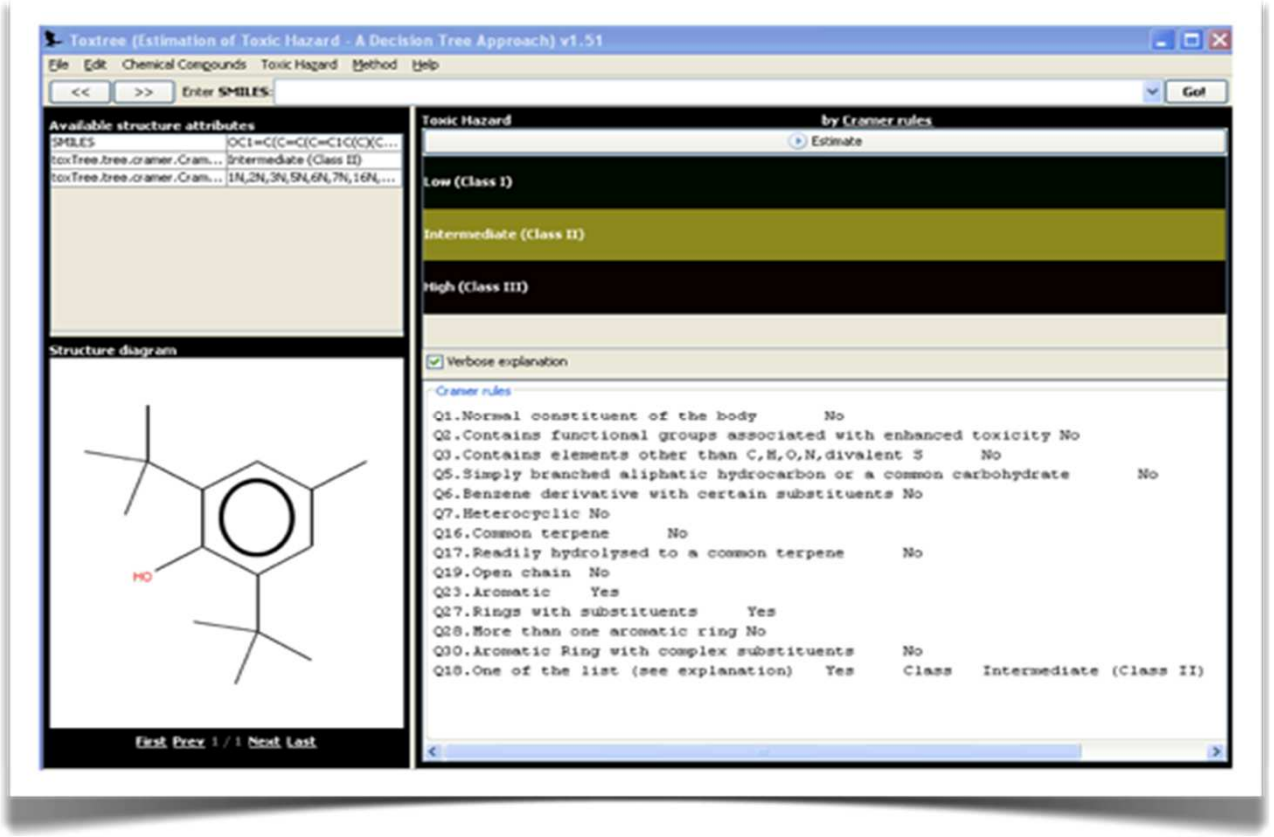
<1.8 mg/person/day

Class II (Medium)

<0.54 mg/person/day

Class III (High)

0.09 mg/person/day



EDI (Estimated Dayly Intake) (mg/person/day)= Mig (mg/Kg) x 3 Kg /day/person x CF

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Conclusions

- The **number of migrants** from **packaging materials** can be very high.
- There are **analytical tools** for studying the packaging materials, BUT a combination of different technologies and instruments is required.
- **High resolution** is an **essential key** for **identification** chemical structures of organic compounds.
- Special care and **critical interpretation** of the data are needed to avoid wrong identification.
- **Databases and libraries** as well as experience are extremmely important for identifying the chemicals.
- **Confirmation** always with certified standards is required.

R+D+i Projects

(the latest ones)

- **NATURALPACK (INTERREG)**
- **MIGRESIVES Project (EU, VI FP, Collective Research Project)**
- **NAFISPACK Project (EU, VII FP)**
- **SAFEMTECH (EU, IAPP, Marie Curie)**
- AGL-04363 and AGL- 2012-37886 (Spanish Ministry of R&D&i)
- 4 INNPACTO Projects (Spain)
- ACTIBIOPACK
- NANOFLEXIPACK
- AGL-2015
- RTI-2018
- (RTC2019-007161-2)
- FOODYPLAST (EU)
- PID2021-123742OB-I00
- TED2021-129138B-C21
- SCPP2100C008568XV0

- Several Companies…

- Instituto de Investigación en Ingeniería de Aragón (I3A)
- Gobierno de Aragón

Grupo GUIA (T53_20R) and
Fondo Social Europeo

GUIA group, University of Zaragoza, Spain

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Thank you very much for the attention

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