# Comprehensive analysis of the total migrate from can coatings:

# Solvents vs. simulants vs. foods

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# What can migrate from FCMs?

- Known ingredients such as monomers, catalysts, solvents, suspension media, additives, etc.

IAS

- Known or unknown isomers, oligomers, impurities, reaction products and breakdown products of these ingredients
- Possible contaminants from the manufacturing process such as recycled materials, irradiated products, etc.
- Contamination from indirect sources such as printing inks, external coatings, adhesives, secondary packaging, etc.

NIAS

# How can we measure IAS and NIAS?

SOLVENTS

- Worse case (?) extraction from FCM
- Determine the NIAS present with the potential to migrate
- Range of solvents can extract a range of NIAS in varying amounts

FOOD SIMULANTS

- Range of simulants cover all food/beverage types
- Designed to over-estimate migration from plastic

FOODS AND BEVERAGES

- Results obtained for migration into food prevails over results obtained in food simulants
- Any results are specific to only that food type and any processing conditions used

# Case studies – Can coatings

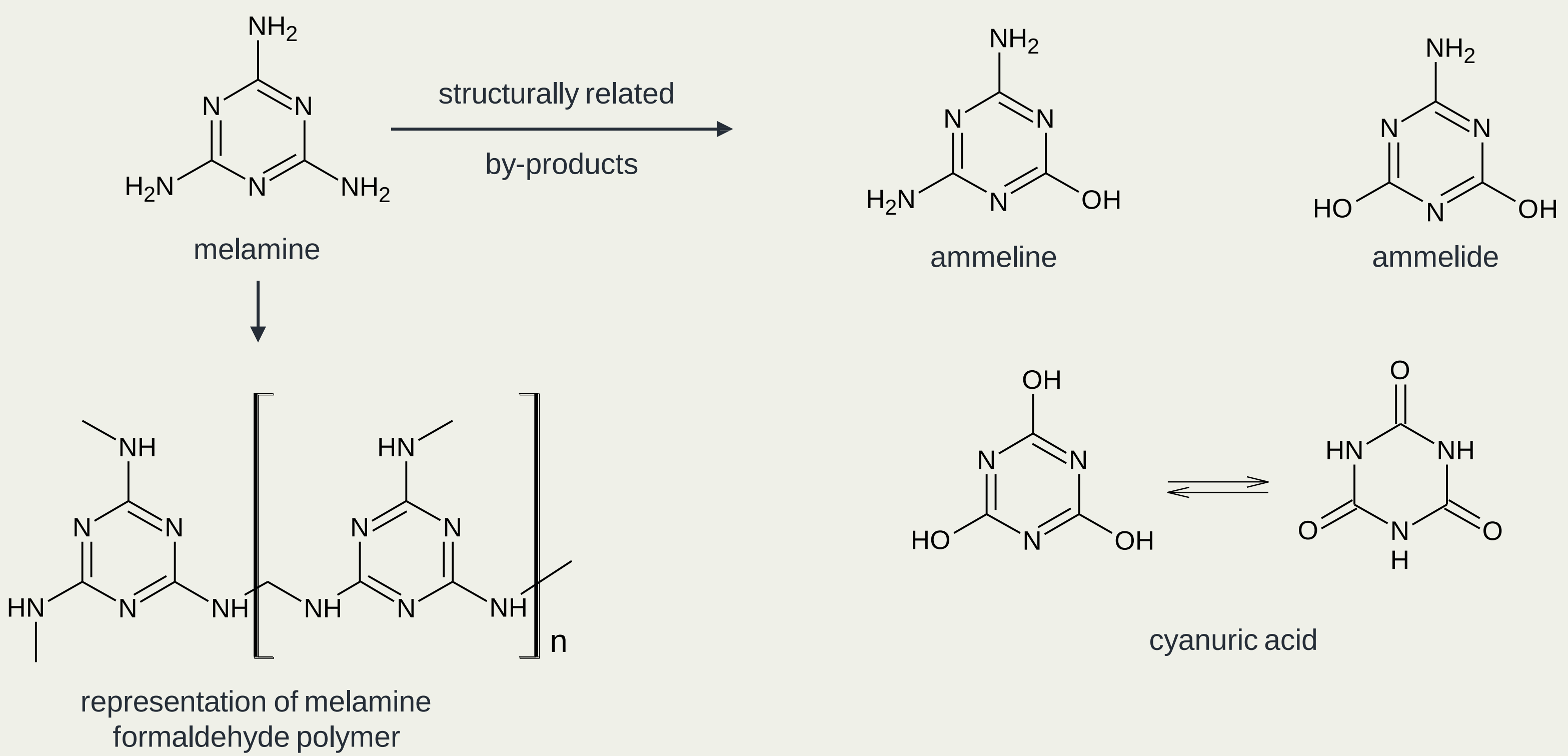
- Comments and considerations when looking at IAS and/or NIAS following extraction with solvents, and/or migration into simulants and/or foods

- Series of case studies involving analysis of can coatings
  1. Migration of melamine from can coatings cross-linked with melamine-based resins, into food simulants and foods
  2. A method of test for residual IPDI trimer in new polyester-polyurethane coatings on light metal packaging using LC-MS/MS
  3. The determination of a monomer extracted/migrating from polyester-based can coatings into solvents, simulants and foods
  4. The determination of monomers and oligomers from polyester-based can coatings into foodstuffs over extended storage periods

# Internal coatings in food cans

- Act as a barrier between the metal of the can and the food
  - Need to be chemically resistant during sterilisation processes and mechanically flexible enough to enable manufacture
  - Also need to be safe for contact with food and beverages
- Ingredients may include resins (monomers and oligomers), cross linking agents, catalysts, lubricants, wetting agents, solvents
  - Potential for these components, impurities, or reaction and degradation products (NIAS) to migrate from the coating into food

# Case study 1 – Migration of melamine from can coatings cross-linked with melamine-based resins into simulants and foods




*Food Additives and Contaminants*
Vol. 28, No. 2, February 2011, 243–250

# Aims and experimental set-up

- Aims of study included
  - Determination of migration levels of melamine (and related substances) from can coatings into simulants and foods
  - Investigation of factors influencing the migration process
- Exposed 13 commercial coatings to food simulants
  - JIG including CIAA, EMPAC, CEPE and other European Manufacturers
  - 10% aqueous ethanol, 1 hour at 130°C and 3% aqueous acetic acid, 1 hour at 100°C – realistic industrial heat processing conditions
- Valspar prepared experimental coatings
  - 10% aqueous ethanol and 3 foods – acidic, fatty and meat/fish
  - Range of t/T conditions
- Simulants analysed directly by LC-MS/MS, foods were extracted with solvent and then analysed

# Results and conclusions - simulants

- Exposed simulants from 13 commercial coatings tested
  - 4 out of 13 samples - melamine <LOD (1 µg/kg)
  - Melamine highest migration levels - 332 µg/kg (10E) and 102 µg/kg (3AA)
  - Cyanuric acid <LOD (20 µg/kg) in all cases
  - Ammelide <LOD (5 µg/kg) in all cases
  - Ammeline detected in 1 sample at 8 µg/kg, all others <LOD (5 µg/kg)

- Migration greater into 10E than 3AA – believed to be temperature effect rather than difference in simulant properties
- Migration into simulants (reported here) were greater than levels of residual content by solvent extractions (reported elsewhere) suggesting degradation of coating by hydrolysis

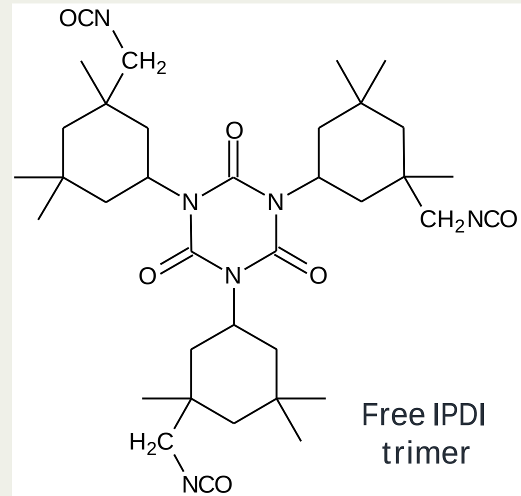
# Results and conclusions – simulants vs food

| Food or simulant | Industry T/t | Lab T/t | Melamine migration (µg/kg) |
|---|---|---|---|
| **Acidic food** | low/long | | <23 |
| 10% ethanol | low/long | | 28 |
| | | 109°C/60 minutes | 32 |
| | | 109°C/90 minutes | 32 |
| **Fatty food** | medium/long | | 57 |
| 10% ethanol | medium/long | | 87 |
| | | 121°C/60 minutes | 68 |
| | | 121°C/90 minutes | 68 |
| **Meat/fish** | high/short | | 38 |
| 10% ethanol | high/short | | 63 |
| | | 134°C/20 minutes | 66 |
| | | 134°C/60 minutes | 98 |

- Agreement between samples processed in Industrial setting and the lab
- Some agreement between food and simulant migration values
- Temperature seems to have a greater effect on migration than food/simulant composition

# Case study 2 – Residual IPDI trimer in new polyester-polyurethane coatings on light metal packaging using LC-MS/MS

- Polyester-polyurethane based experimental coatings containing IPDI trimer
- Extraction and derivatisation with DBA followed by LC-MS/MS analysis
- IPDI trimer seen to extract into acetonitrile (levels between 0.6 and 12 µg/6 dm$^2$)
- What is the fate of IPDI trimer if it was to migrate into foods?



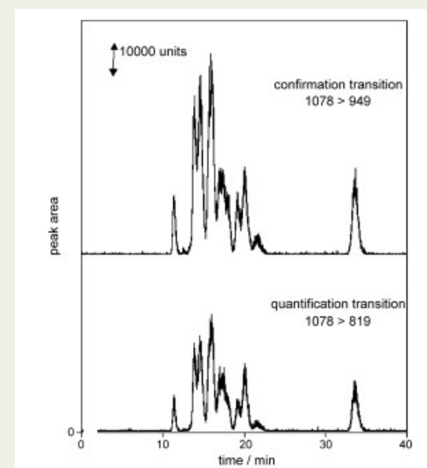
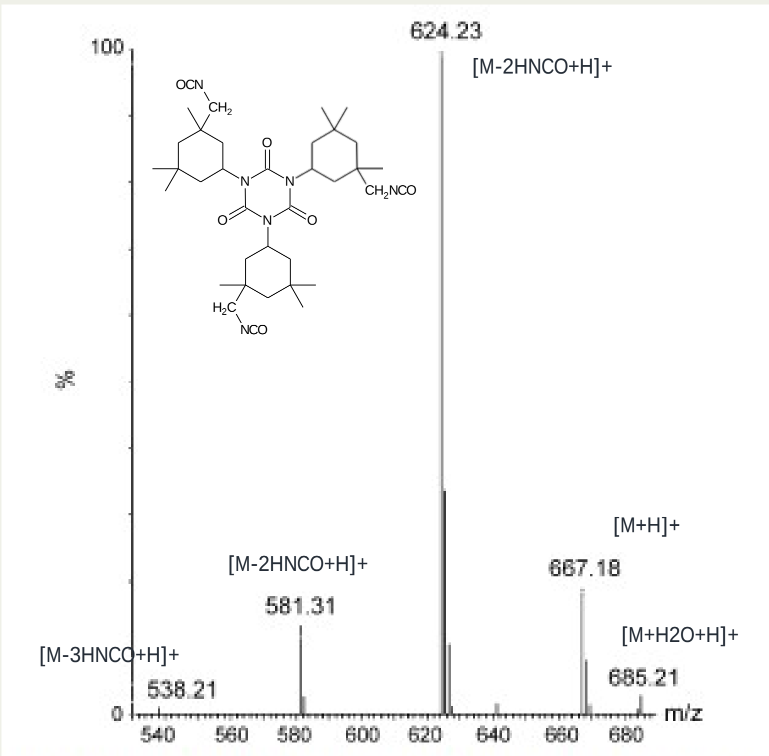




Fig. 2. LC–MS/MS traces for standard IPDI trimer (75 ng/mL) derivatised with DBA.

Journal of Chromatography A, 1141 (2007) 61–66

# IPDI trimer fate in water




Mass spectra of:

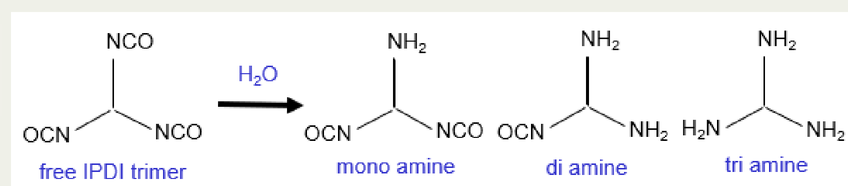
- IPDI trimer
- IPDI trimer + water

  (21$^{o}$C for 5 minutes)

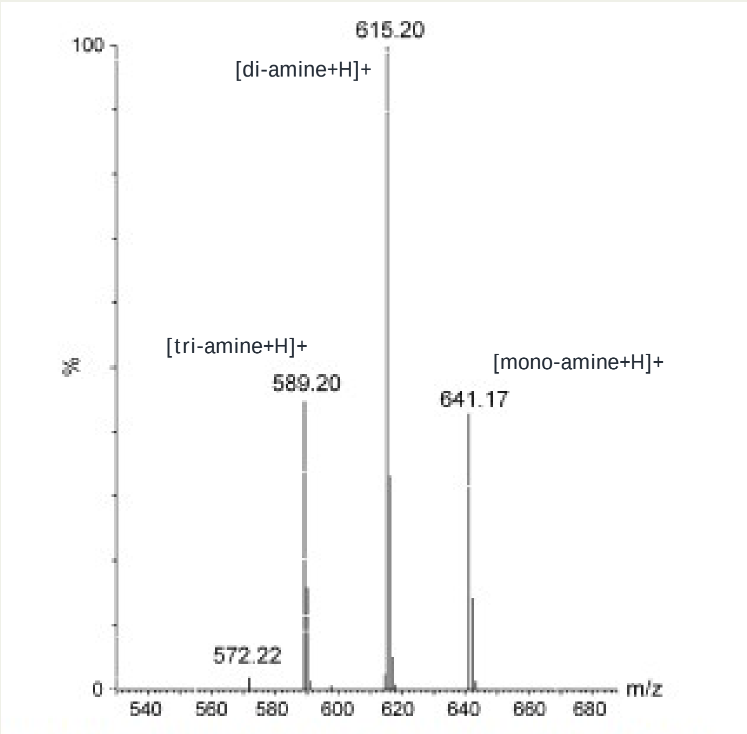
- IPDI trimer + water

  (50$^{o}$C for 1 hour)

all showed evidence for free IPDI trimer only and no hydrolysis products



# IPDI trimer fate in water




Partially hydrolysed IPDI trimer

Mass spectrum of:

- IPDI trimer + water

  (21°C for 72 hours)

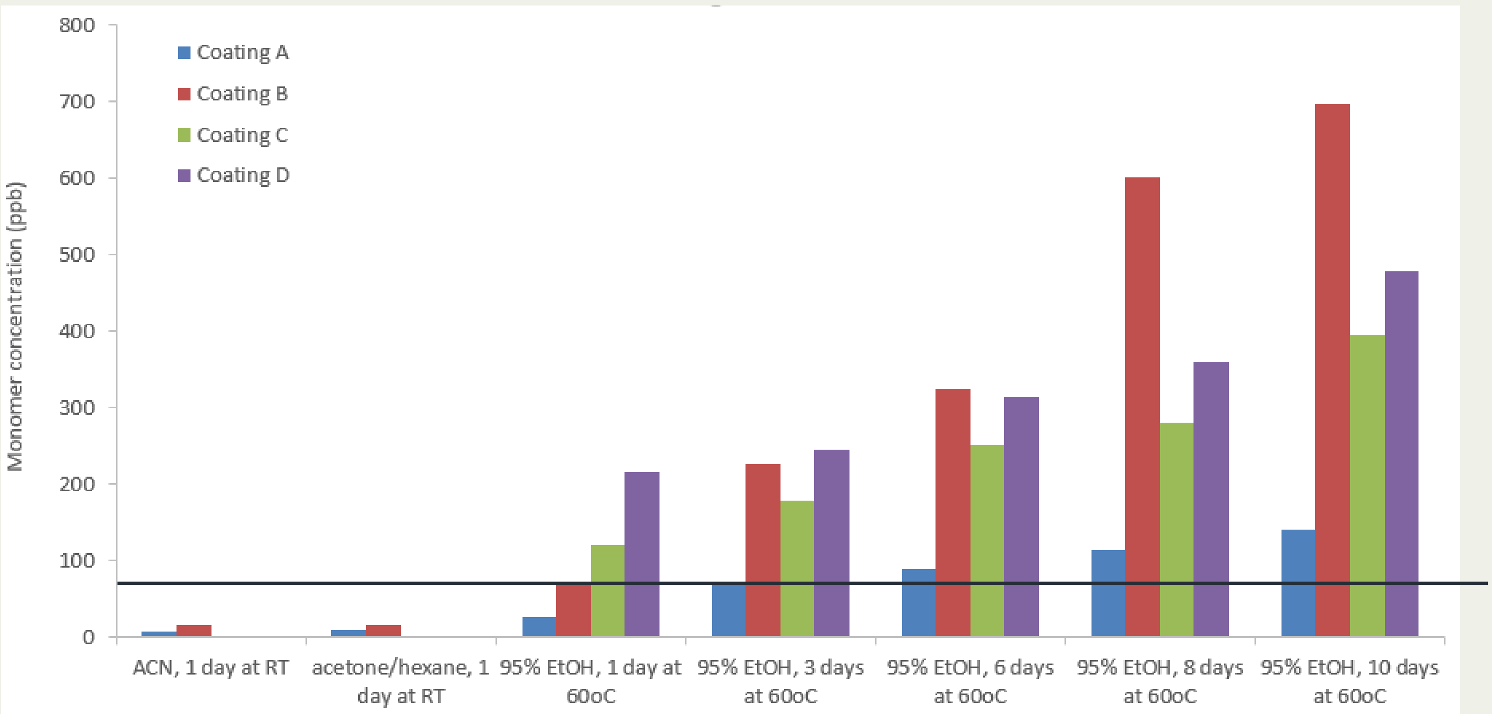
showed NO evidence for free IPDI trimer and presence of the 3 hydrolysis products – aliphatic amines

# IPDI trimer fate in canned oil

- Sunflower oil canned and processed under usual industrial conditions (121$^{o}$C for 50 minutes) in cans coated with IPDI trimer based coating
  - Extracted, derivatised and analysed by LC-MS/MS
  - Sample over-spiked with IPDI trimer prior to extraction
- IPDI trimer not detected in sunflower oil (<1.8 µg/kg)
- Recovery 34% - evidence of poor extraction from oil and/or hydrolysis of over-spiked IPDI trimer

- Conclusion – Even if IPDI trimer migrated into aqueous or fatty food/simulant then expect full hydrolysis of isocyanate groups to aliphatic amines

# Case study 3 – The determination of a monomer extracted/migrating from polyester-based can coatings into solvents, simulants and foods



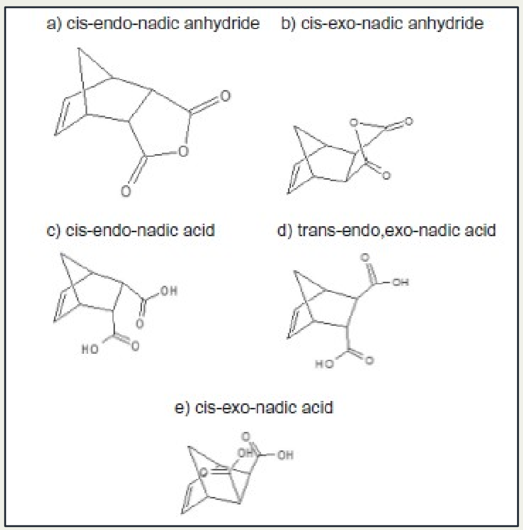

Monomer measured at <68 ppb in mayonnaise stored in coated tubes

Use of 95% aqueous ethanol over-estimates migration into mayonnaise

Data not published

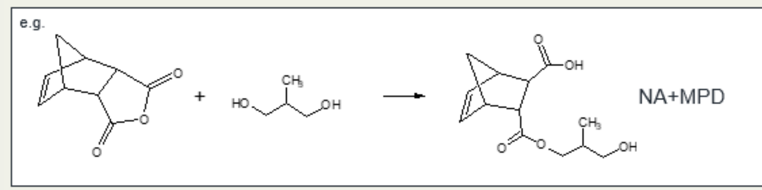
# Case study 4 – The determination of monomers and oligomers from polyester-based can coatings into foodstuffs over extended storage periods

## Monomers based on:




LC-MS/MS and GC-TOF-MS

## Oligomers predicted based on knowledge of ingredients




| | | AA | TMA | PA | CHDM | BD | EG | DEG | PG | HD | HMP | TMP | NPG | H2O | MW |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PA+EG | linear | | | 1 | | | 1 | | | | | | | 1 | 210.0528 |
| EG+PA+EG | linear | | | 1 | | | 2 | | | | | | | 2 | 254.0790 |
| PA+EG+PA+EG | linear | | | 2 | | | 2 | | | | | | | 3 | 402.0951 |
| PA+EG+PA+EG | cyclic | | | 2 | | | 2 | | | | | | | 4 | 384.0845 |
| PA+EG+PA+EG+PA | linear | | | 3 | | | 2 | | | | | | | 4 | 550.1111 |
| PA+EG+PA+EG+PA+NPG | linear | | | 3 | | | 2 | | | | | | 1 | 5 | 636.1843 |
| PA+EG+PA+NPG+PA+EG | linear | | | 3 | | | 2 | | | | | | 1 | 5 | 636.1843 |
| PA+PG+PA+PG+PA+PG | linear | | | 3 | | | | | 3 | | | | | 5 | 636.1843 |
| PA+PG+PA+PG+PA+PG | cyclic | | | 3 | | | | | 3 | | | | | 6 | 618.1737 |

LC-TOF-MS


FOOD ADDITIVES & CONTAMINANTS: PART A, 2018
https://doi.org/10.1080/19440049.2018.1440643

# Experiments carried out

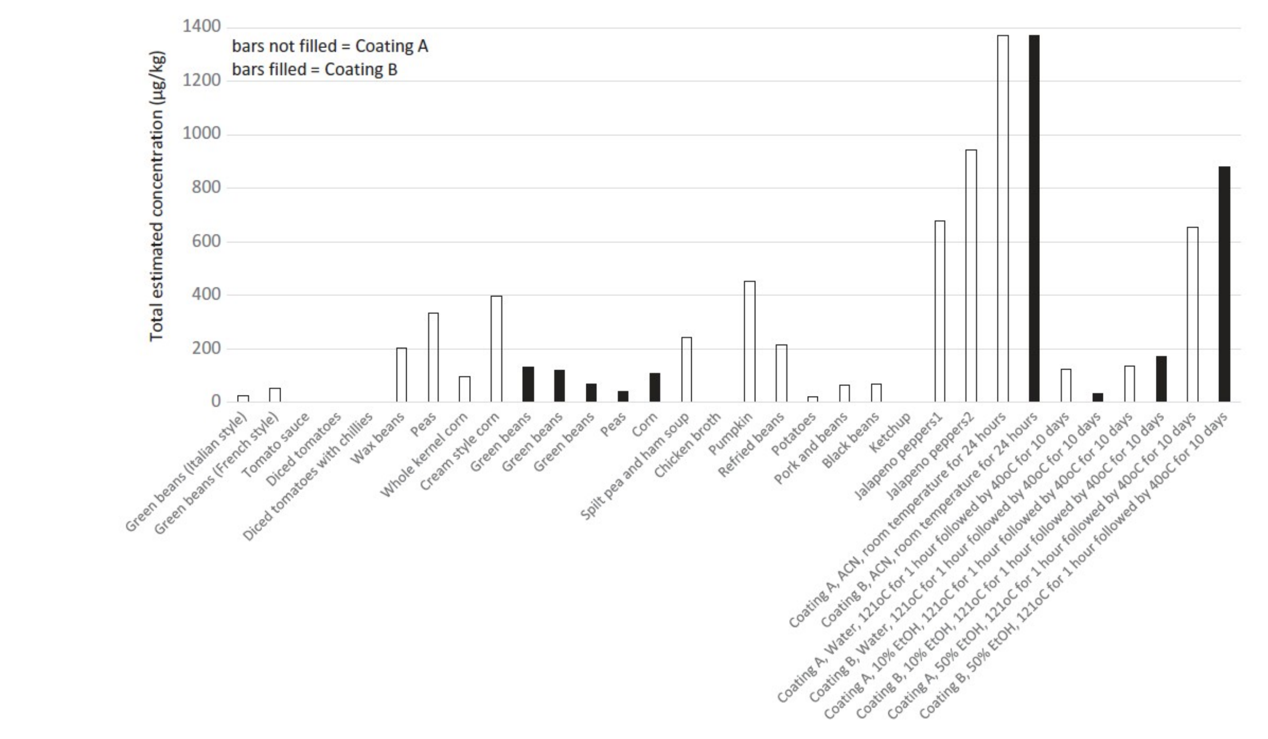
- Foods covering different
  - Commodities
  - pH values
  - Coatings
  - Coating layers
  - Storage times
- Simulants
  - Water
  - 10% aqueous ethanol (v/v)
  - 50% aqueous ethanol (v/v)
  - 121°C for 1 hour followed by 10 days at 40°C
- Solvent
  - Acetonitrile
  - Room temperature, 24 hours

| # | Food type | Number of cans tested | Coating | pH value | Age of food at extraction (months) |
|---|---|---|---|---|---|
| 1 | Green beans (Italian style) | 3 | A | 5.2 | 20 |
| 2 | Green beans (French style) | 3 | A | 5.2 | 23 |
| 3 | Tomato sauce | 3 | B | 4.0 | 38 |
| 4 | Diced tomatoes | 4 | B | 4.2 | 35 |
| 5 | Diced tomatoes with chillies | 4 | B | 4.0 | 36 |
| 6 | Wax beans | 4 | A | 5.5 | 14 |
| 7 | Peas | 6 | A | 6.0 | 14 |
| 8 | Whole kernel corn | 4 | A | 6.9 | 14 |
| 9 | Cream style corn | 2 | A | 6.3 | 13 |
| 10 | Green beans | 6 | B | 5.2 | 15 |
| 11 | Green beans | 8 | B | 5.2 | 28 |
| 12 | Green beans | 4 | B | 5.2 | 26 |
| 13 | Peas | 4 | B | 6.0 | 28 |
| 14 | Corn | 4 | B | 6.3 | 27 |
| 15 | Spilt pea and ham soup | 4 | A | 5.8 | 30 |
| 16 | Chicken broth | 8 | B | 6.9 | 30 |
| 17 | Pumpkin | 4 | A | 5.9 | 18 |
| 18 | Refried beans | 2 | A | 6.0 | 18 |
| 19 | Potatoes | 2 | A | 5.9 | 18 |
| 20 | Pork and beans | 2 | A | 5.4 | 33 |
| 21 | Black beans | 1 | A | 6.0 | 33 |
| 22 | Ketchup | 1 | A | 4.0 | 43 |
| 23 | Jalapeno peppers[a] | 4 | 2xA[c] | 3.3 | 8 |
| 24 | Jalapeno peppers[b] | 4 | 2xA[c] | 3.3 | 8 |

[a]Stored at room temperature.
[b]Stored at 38°C.
[c]Indicates double coat, all others are single.

# Results – Monomers and oligomers

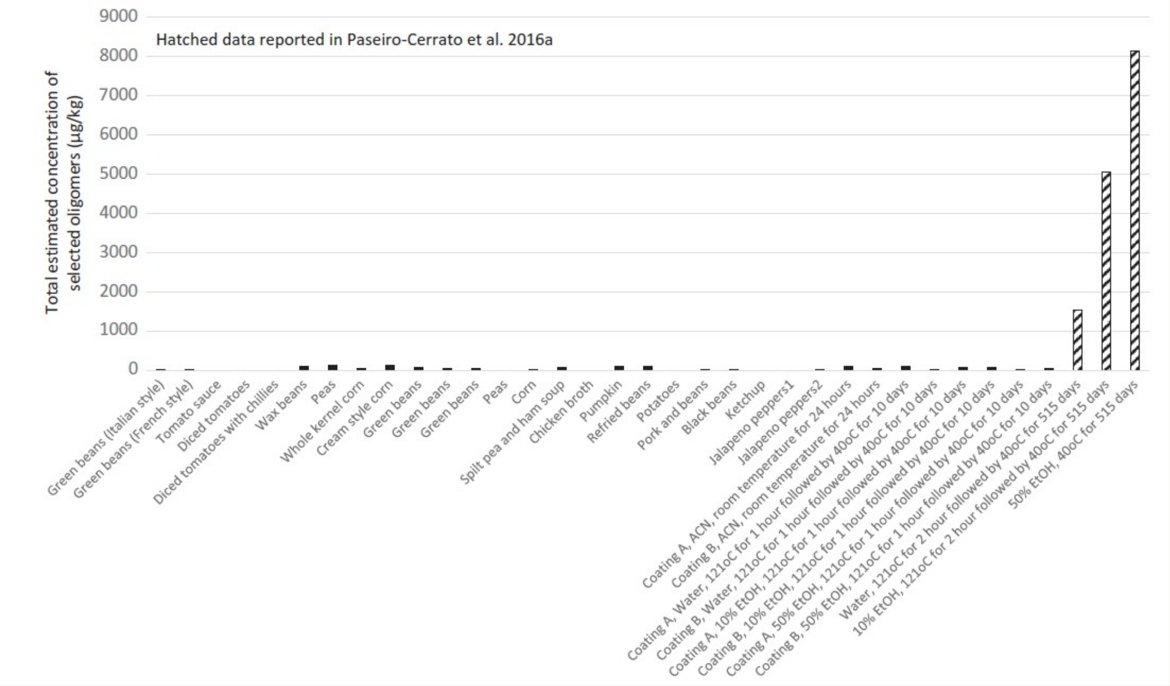
- On the whole, migration of monomers into foods did not exceed 50 µg/kg (2 exceptions)
- Theoretical oligomers (database matches):




Estimated concentration of total oligomers in foodstuffs, acetonitrile and simulants

# Comparison to other reported data

- Paseiro-Cerrato et al. (J. Agri. Food Chem. (2016) 64, 2377-2385) tested polyester coated cans similar to those in our study
- Long term migration test using food simulants retorted and stored at 40°C for up to 515 days - Concentration of oligomers determined




Estimated concentration of selected oligomers in foodstuffs, acetonitrile and simulants, compared to reported FDA data

# Conclusions of Case Study 4

- The were no obvious trends in monomer or oligomer levels associated with typical characteristics of foodstuffs (for example fatty, acidic), therefore it is necessary to determine levels in the foodstuffs of interest
- Migration of oligomers into 50% aqueous ethanol held at 121$^{o}$C for 1 hour followed by 10 days at 40$^{o}$C, was higher than that into foods
- The migration levels determined in foodstuff following long term storage were significantly lower than those reported for simulants exposed to a similar coating following long term storage and therefore question the suitability of those conditions to represent realistic migration

# Summary of all case studies

- Evidence that
  - Solvent extraction does not always represent worse case migration
  - Simulants can be used successfully to represent foods in some migration studies

  BUT
  - Simulants can over-estimate migration into food in other cases

- Each case needs to be assessed based on the chemistry of the coating system, the food types intended to be used and the conditions of storage envisaged

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