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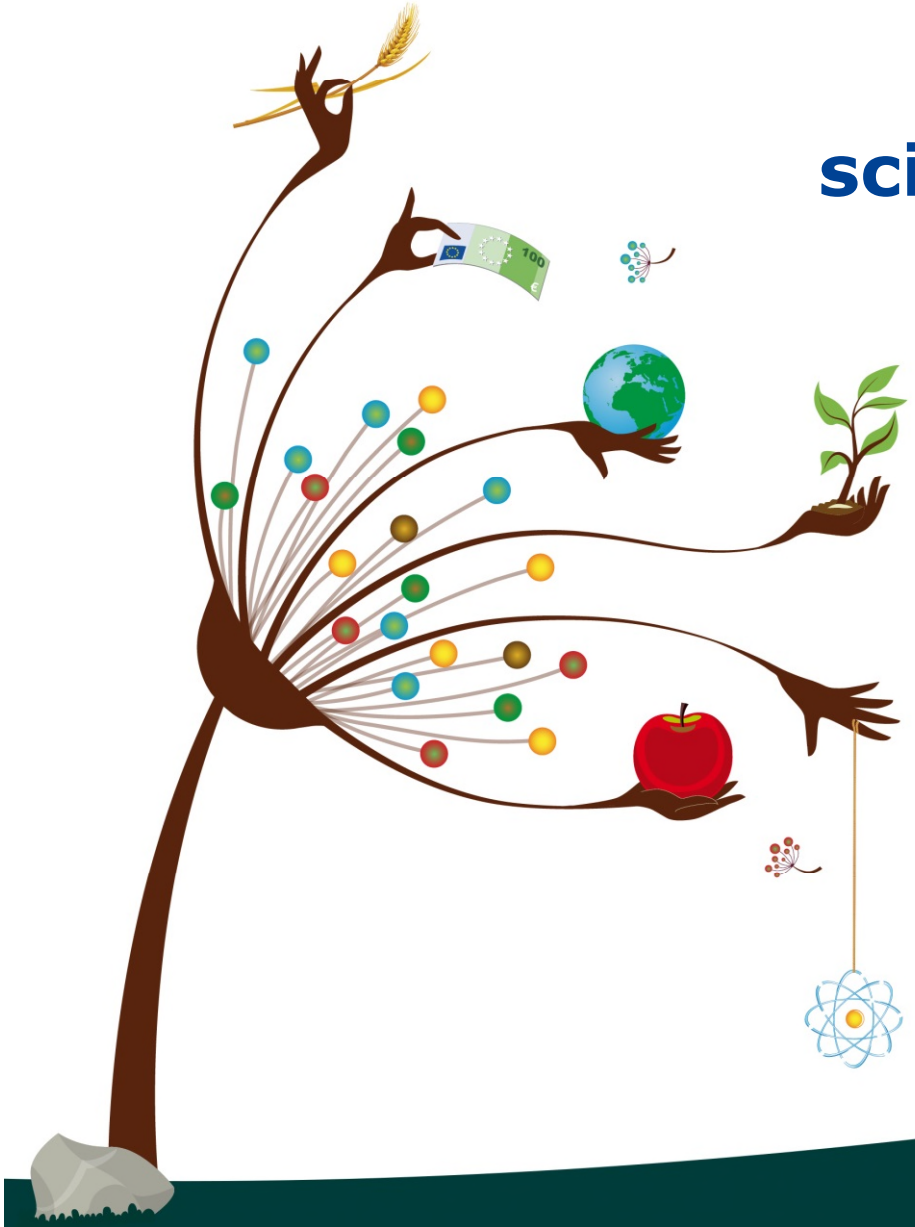

The European Commission's science and knowledge service

Joint Research Centre

JRC scoping investigations on release of metals from ceramics ware, crystal ware and bakeware in foodstuffs in support of potential future risk management initiatives

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EFSA FIP Network 24-26 May 2016

Joint Research Centre

JRC work towards development of policies: example of ceramics

- **Ceramics: 1985, only 2 metals (release Pb and Cd)**
- **New: rim, crystal, bakeware, 10 metals, lower limit**
- **Solve technical questions BEFORE policy discussion**
  - What can migrate? New testing approaches?
  - Simulations at room temperature possible for bakeware?
- **Key= collaborations with stakeholders (>4500 tests)**
- **Goal: pragmatic options (food safety, trade, feasibility)**

Overview of work development

➢ Analytical side:

- ILC on 8 metals and 55 participants fed into ISO TC 166
- Equivalencies of ICPMS, OES, AAS for quantification at lower levels and for more metals.

➢ Development comparisons of test

- Comparisons of testing regimes
- Rim test comparing standards
- Repeat migrations: investigation of weekend gaps
- Occasional vs. frequent use: effect on release of Pb for crystal
- Development of tests for bakeware (food real use vs. conventional testing)

➢ Mixed stakeholder open group

ILC

Exercises 55 participants

2014: 2ILCs on quantification of Elements released from food contact materials

- Plastic (Ba, Co, Cu, Fe, Mn, Zn, Li, Sb) -SMLs from Regulation 10/2011
- Ceramic (Ba, Co, Mn, Pb, Cd, Ni, As, Al) from DSV-BfR-CoE suggested values

2015: precision criteria,

- including reproducibility and repeatability for metals in acidic migration solutions.

Results

- **Proficiency test:**
  - >90 % satisfactory score for set of 7 metals
- **Precision criteria :**
  - analytical techniques (ICP-MS, ICP-OES, AAS*) equivalent for all elements tested

** Note: Includes ETA-AAS GF-AAS F-AAS*

	DIN 38402 A45/ISO 5725-5						
Sample				C2			
Element	Ba	Co	Mn	Pb	Cd	Ni	Al
ICP-MS/ICP-OES Test decision	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences
ICP-MS/AAS Test decision	-	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	-
ICP-OES/AAS Test decision	-	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	-

Next steps

- ✓ Gave the method to ISO TC 166
- ✓ Gave the analysis of precision criteria to ISO TC 166
- ✓ Contributed to writing the protocol for ICP MS

Ceramics release and testing

- **Previous work**
  - comparisons different tests (citric acid, acetic acid, accelerated tests)
  - Rim test comparing standards
  - Release on crystalware
- **Current work**
  - Repeat migrations: investigation of weekend gaps
  - Occasional use vs. frequent use: effect on release of lead from crystal
  - Development of tests for bakeware
    - *comparative conventional tests and kinetics in boiling tomato*

RIM studies– results

- **slight differences observed between ISO and ASTM standards**
  - official methods used: EN 1388-2; ISO 6486-1; ASTM C927-80
  - ISO uses wax on the non-tested portion of article
  - use of the EN1388-2:1995 and ISO standards more appropriate

- **Who is doing what?**
  - most of the laboratories have validated and accredited methods for: Pb and Cd
  - 24 out of 37 are lip/rim tests
  - 19 out of 24 are using melted paraffin wax

Ceramics and glassware – migration tests covered in the current work

- Acetic acid 4% , 24 h @ 22°C
- White wine
- Tomato sauce
- Kinetics
- Investigation of 3 successive migrations

Ceramics – repeat use and weekend gap

Premise: 3 migrations

- Limitations on starting days for laboratories?
  - May imply a period of "rest" between consecutive tests
- Need to ensure a lag phase between test may not have a significant impact on the release in the context of a compliance test.

Approach

- Evaluation repeat use with a 2 day gap between successive test (1st-2nd migration or 2nd-3rd migration) with 2 protocols compared
  - to leave article empty or
  - filled with tap water.
  - Compared to 3 successive migrations

- Test samples: 4 higher releasing test articles (each 4 specimens)

Conclusions

Consecutive tests vs		NO SIGNIFICANT DIFFERENCE			
		Tests with the weekend gap between			
		1st and 2nd migrations		2nd and 3rd migrations	
		H_2O	No H_2O	H_2O	No H_2O
Pd	mortar	NO	YES	YES	YES
	bowl	YES	YES	NO	YES
	cup	NO	YES	NO	YES
	plate	YES	YES	YES	YES
Cd	cup	YES	YES	YES	YES
Ba	mortar	YES	NO	YES	YES
	bowl	YES	YES	YES	YES
	cup	NO	NO	YES	NO
	plate	YES	YES	YES	YES
Co	bowl	YES	YES	YES	YES
	cup	YES	YES	NO	NO
	plate	YES	YES	NO	YES
Mn	bowl	YES	YES	YES	YES
	cup	YES	YES	NO	YES
	plate	YES	YES	YES	YES
Al	mortar	YES	NO	YES	YES
	bowl	YES	YES	YES	YES
	cup	YES	NO	NO	NO
	plate	YES	YES	YES	YES
Li	bowl	YES	YES	YES	YES
	cup	YES	NO	NO	NO
Ti	bowl	YES	YES	YES	YES
	cup	YES	YES	NO	YES
	plate	YES	NO	NO	NO
Zn	bowl	YES	YES	YES	YES
As	mortar	YES	YES	YES	YES
	bowl	YES	YES	YES	YES
	cup	YES	YES	NO	NO
	plate	YES	YES	YES	YES
Ni	cup	YES	YES	NO	NO
	plate	YES	YES	YES	YES

- **Limited set of samples (4)**
- **No difference of Pb/Cd between 3 consecutive tests and tests with weekend gap IF LEFT EMPTY**
- **Repeat use testing can be done even with weekend in successive migration testing (1-2 or 2-3)**
- If results close or above compliance then 3 strict successive migration test would be needed for confirmation

LEAD CRYSTAL investigations

Second phase of experiments

- **Migration test of 24 h @ 22°C used for ceramics could be too severe taking into account the different final use of crystal glass articles**

- **Need test to mimic short-term contacts under realistic consumer use for crystal glass products**

- **Repeat use test conditions need to be considered**
- **Migration test should be pragmatic**

Crystal ware – migration tests

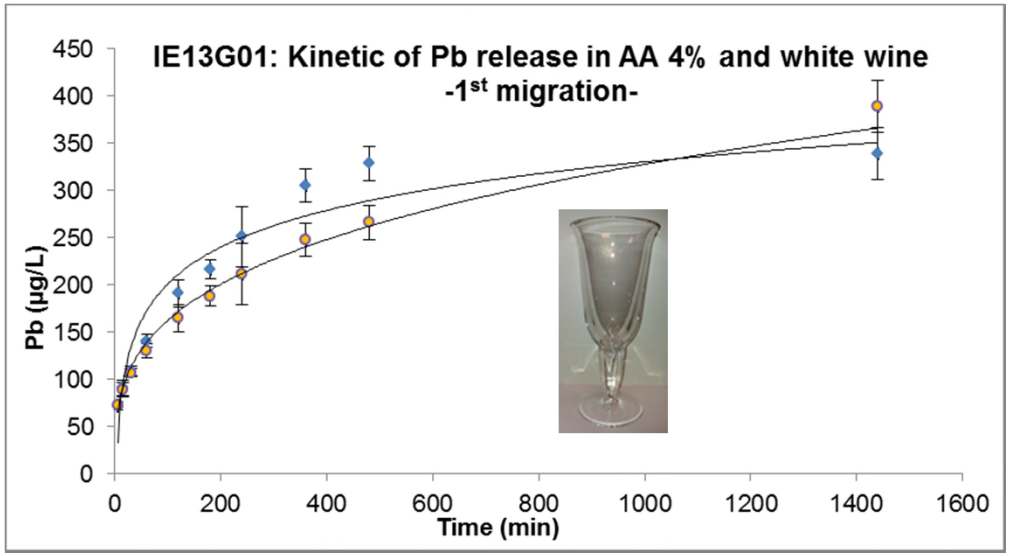
1st set of experiments

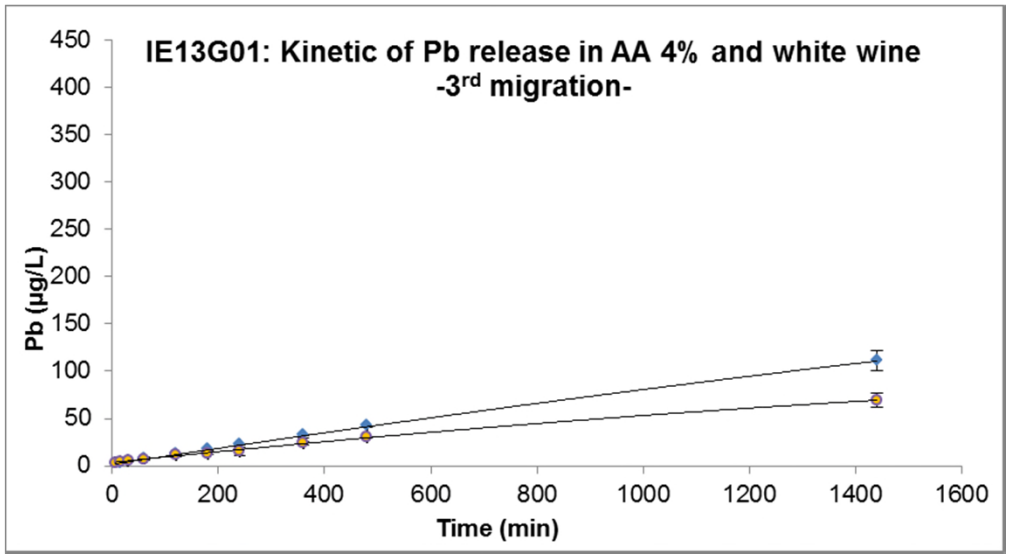
- Acetic acid 4%, 24 h @ 22°C
  - ➔ **Aliquots at 5, 15, 30, 60, 120, 180, 240, 360, 480, 1440min (+replenish)**
  - ➔ **3 consecutive kinetics**

2nd set of experiments – different migrations tests

- Acetic acid 4% @ 22°C
  - ➔ **3 migrations of 0.5 hour**
  - ➔ **3 migrations of 1 hour**
  - ➔ **3 migrations of 2 hours**
  - ➔ **3 migrations of 24 hours**
- White wine (@ 22°C)
  - ➔ **3 migrations of 4 hours**
  - ➔ **3 migrations of 24 hours**

Example of kinetics results



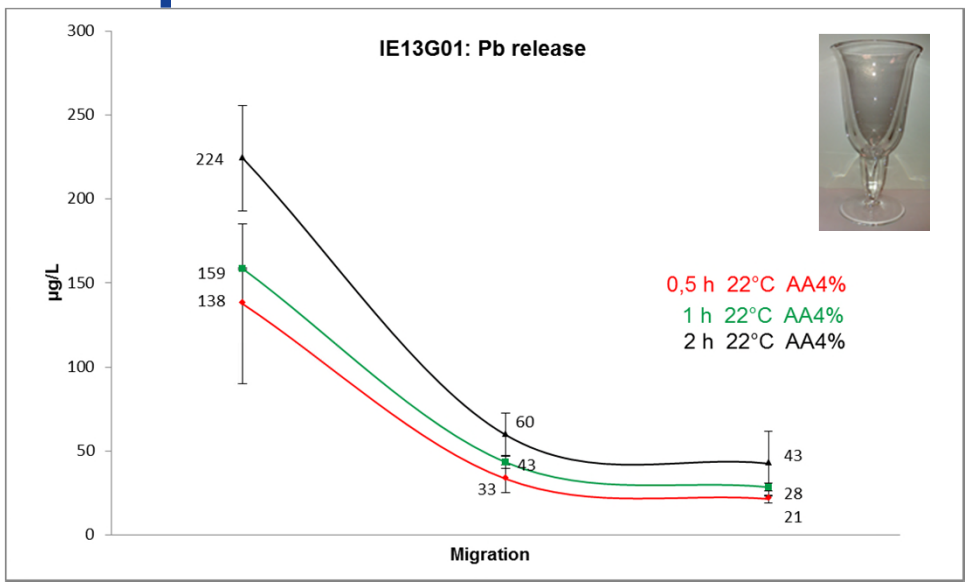


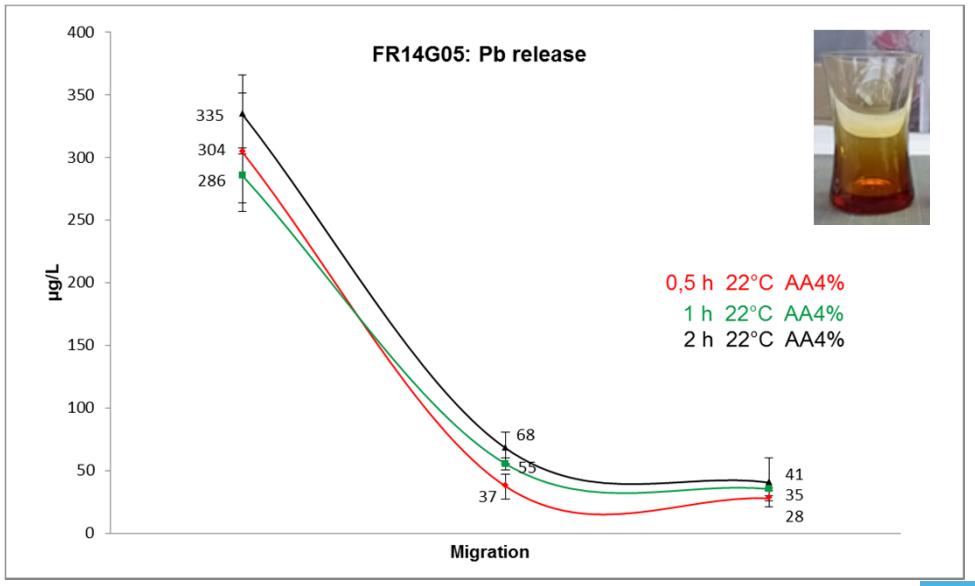
Acetic acid 4%
White wine

- **The majority released in 1st migration**
- **Release behaviour in AA4% and wine fairly similar**
- **3rd migration quite low vs. 1st one (both in simulant and in wine)**

Multiple repeat use study in white wine confirmed the rapid decrease of Pb release upon 1-3rd exposures and stabilisation after 4th exposure (not shown- relation to exposure).

Examples of short test results





Development of conventional tests in simulant

- Conventional test (24hr 22C, wine + simulant): is unrealistic both with wine and with simulant.
- Not appropriate to use ceramics testing for crystal
- Shorter time tests (0.5, 1, 2 hours), repeat use, AA 4%:
- a test with 2 hours repeat test: adequate + possible in 1 work day

Storage effect studies (release in occasional use): results suggest that for articles used only few times per year, a repeat use test regime will NOT be representative (release "refreshed" back to 1st migration levels)

Cookware and bakeware






- ✓ Articles of category 3ª (84/500/EEC)

Experimental design

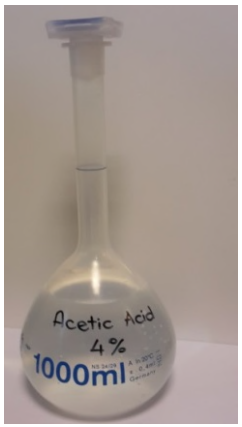
3 Kinetics in benchmark food at high temperature (considering real use)

Slow boiling till 6 hours

Preparation - 4 units cleaned with detergent*,rinsed (tap + Milli-Q water)

3 Migration tests using food simulant Acetic Acid 4%

24 hours at 22°C



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Kinetics in foodstuff

- ✓ Tomato sauce (pH 3.5), slow boiling (6 hours) ➔
  - ✓ 0.5 , 1, 2, 3, 4, 5, and 6 hours; and
  - ✓ 5 g of tomato sauce taken + same amount fresh restored in the bakeware immediately after sampling*
  - ✓ 3 consecutive kinetics

*(*correcting loss of Pb from sampling)*

Migration test with simulant

✓Acetic acid 4%, 22 ºC 24 hours, 3 migrations

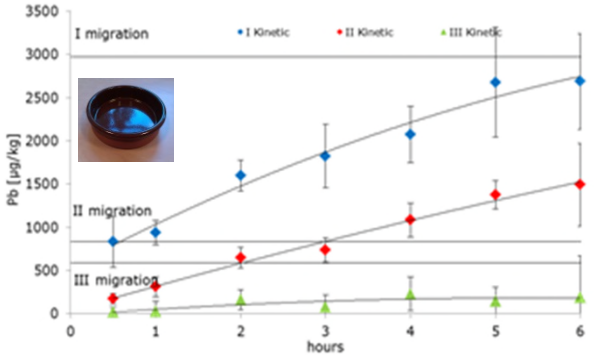
ICP-MS Analysis : sample preparation

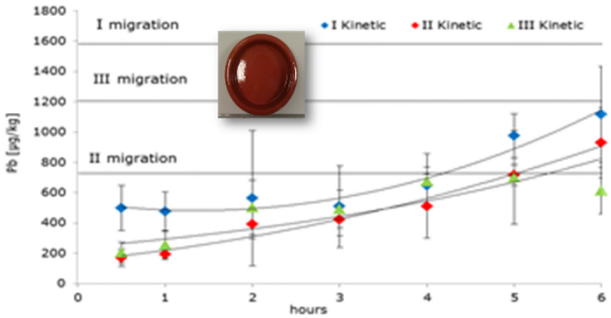
✓ Acetic acid 4% - Dilution at least 1/10 (with Milli-Q) and direct analysis

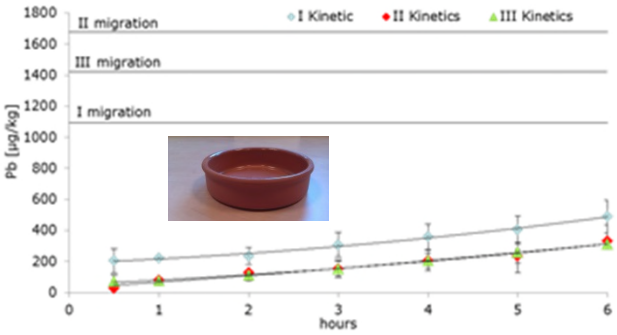
✓ Tomato sauce – 45 minutes Acidic microwave digestion and dilution with Milli-Q

Working with acids is not fun even at room temperature….

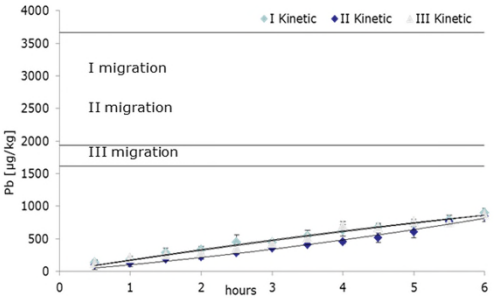
Results

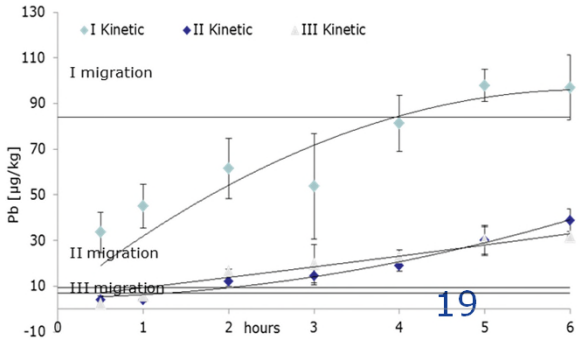






- Different items different behaviours ….
- Relation Pb migration to acetic acid 4% (24 h) and tomato sauce (6 h) is not evident
- Research is on-going
  - More on sauce toward exposure (conditions of use)
  - on options for conventional tests – preferably not using boiling conditions in considerations of operators safety, equipment durability, and energy cost effectiveness.





Conclusions

- Hurdles in repeat testing overcome
- Storage effect identified and quantified (crystal/ceramics)
- "sensitive" articles identified
- Survey planned on occasional use
- Rim work completed

- More work needed on bakeware
- Results on crytalware to present/discuss with stakeholders

- Relation to exposure: data of chemical occurrence generated and available where needed for a large sets of metals from a relevant variety of samples.

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