Joint Research Centre (JRC)

Brominated Flame Retardants in Plastic

A Proficiency Test

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IRMM - Institute for Reference Materials and Measurements

Geel - Belgium

http://irmm.jrc.ec.europa.eu/

http://www.jrc.ec.europa.eu/

International Evaluation Measurement Programme, IMEP®, JRC - IRMM

- Distributes **metrological** traceability
- Assists participants to evaluate their:
  - Measurement **uncertainty**
  - **Interpretation** of the PT results

Stakeholders:

DG SANCO, DG ENTR, EA, APLAC

- **Directive 2002/95/EC**
  on the restriction of the use of hazardous substances in electrical and electronic equipment (***RoHS***)
  and **Decision 2005/618/EC**

- **Regulation (EC) 850/2004**
  on persistent organic pollutants (***POPs***)
  and **Regulation (EC) 756/2010**

  Tolerates 0.1 % b.w. (1 mg kg^{-1})
  (sum PBDEs and PBBs)

Quality control material IRMM-310

Poly(ethyleneterephthalate)

Homogeneity investigated (ISO13528)

Measurands

- Total Br,
- BDE-47, BDE-99, BDE-183, BDE-209, BB-209,
- Total sum of PBDEs
- Total sum of PBBs

Informative values IRMM-310 confirmed

Expert laboratories:

- Vlaamse Instelling Voor Technologisch Onderzoek (**VITO**, Belgium)

  HR-ICP-MS for Total Br, HR-GC-MS for BFRs

- **TÜV Rheinland** Taiwan Ltd (Taiwan)

  GC-MS

- Belgian Nuclear Research Centre (**SCK/CEN**, Belgium, only for total bromine)

  k_0NAA

Reference values (mg kg-1)

k_0NAA

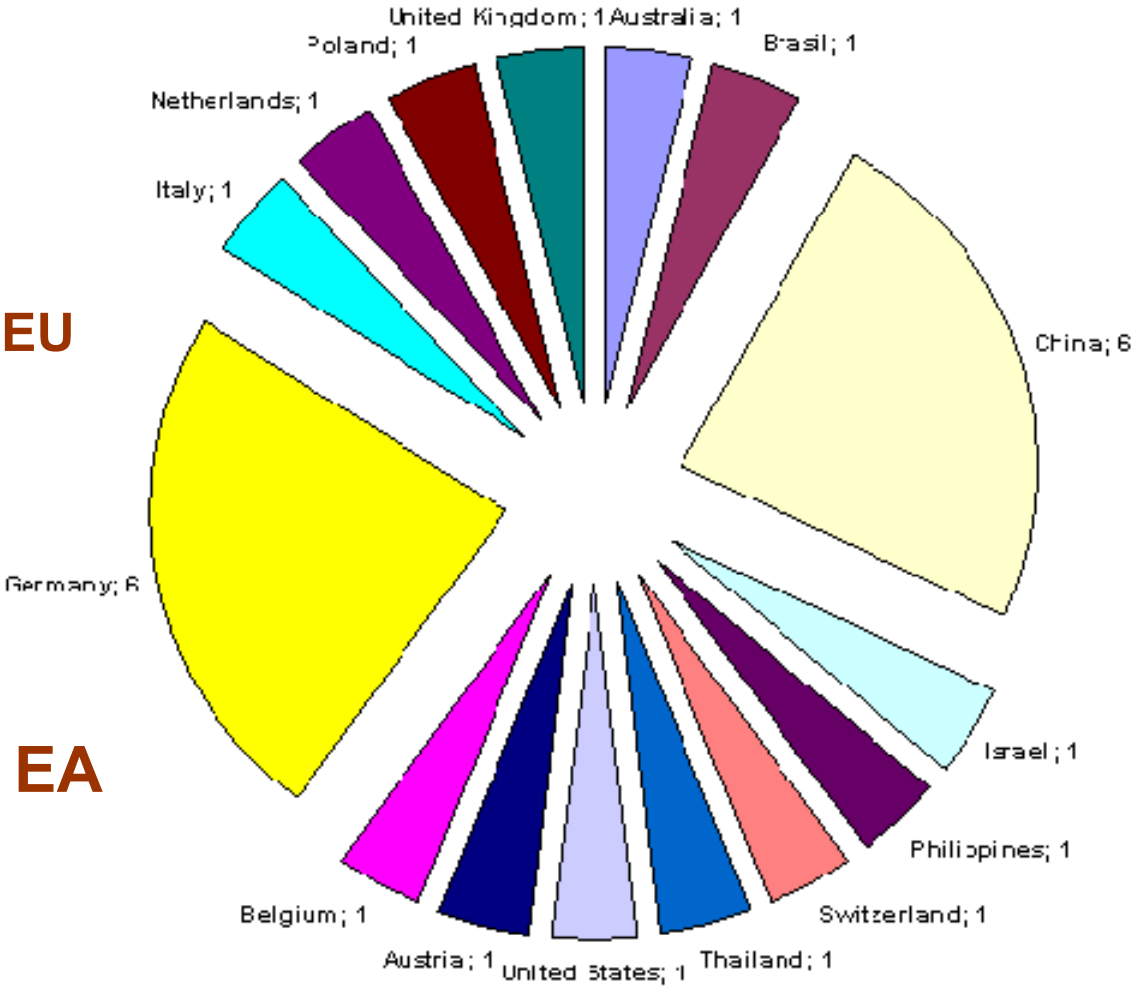
Measurand	VITO Mean ± U	TUV Taiwan Mean ± U	SCK/CEN Mean ± U	IRMM-310 (X ± U)
Total Br	1407 ± 225	1600.1 ± 245	**2245 ± 110**	**2300 ± 120**
Sum of PBDEs	**1507 ± 452**	806.9 ± 7.2		**1800 ± 135**
Sum of PBBs	**825 ± 297**	323.0 ± 7.2		**700 ± 110**
BDE-47	**226 ± 17**	130.3 ± 3.4		**227 ± 25**
BDE-99	**320 ± 45**	168.0 ± 6.2	?	**307 ± 31**
BDE-183	94 + 18	40.2 + 1.4		150 + 17
BDE-209	**728 ± 160**	339.6 ± 9.2		**689 ± 128**
BB-209	**781 ± 281**	323.0 ± 7.2		**700 ± 110**

IRMM-310 values confirmed!

(except for BDE-183, No scoring)

13 labs outside EU

12 labs from EU



25 in total

- **8 nominated by EA**
- **4 from APLAC**

23 reported results

Scoring

- Participants **invited** to report uncertainty

$$z = \frac{x_{lab} - x_{ref}}{\sigma}$$

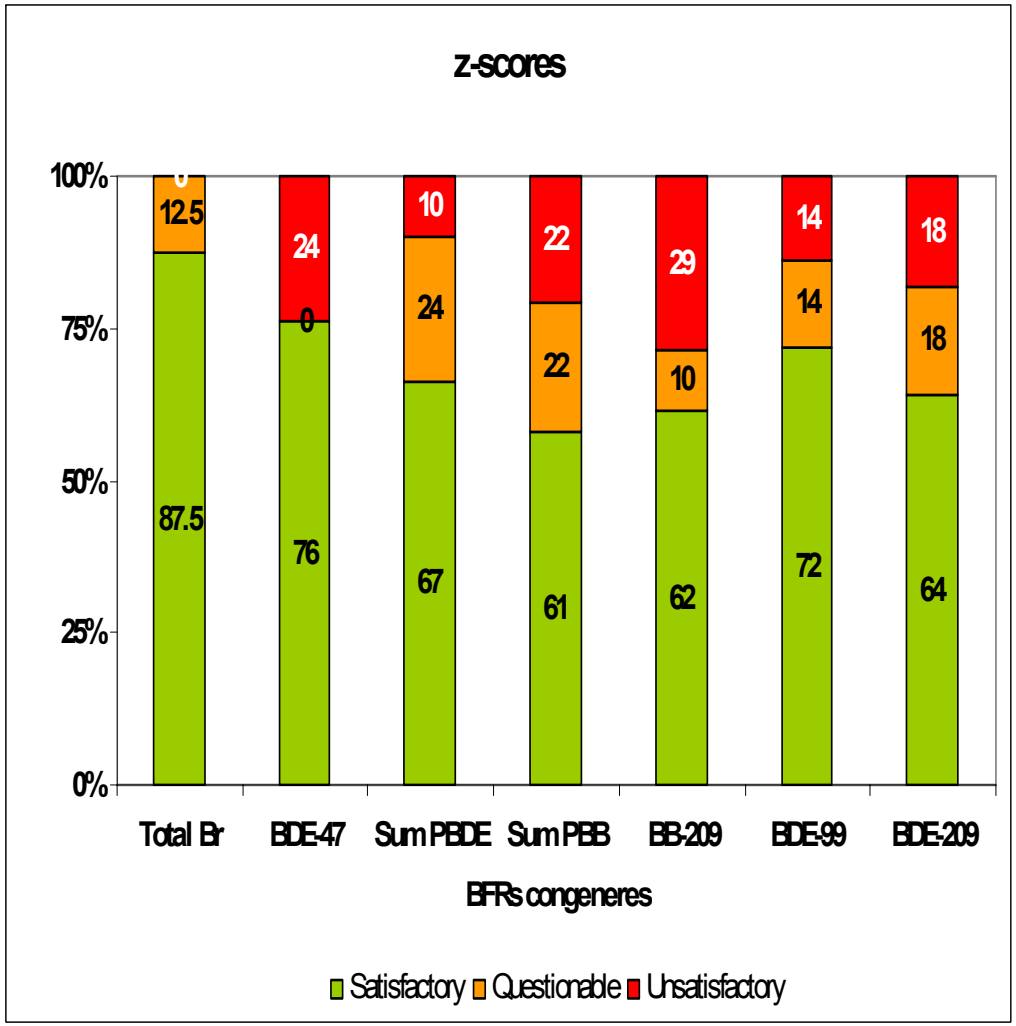
indicates degree of compliance with peers, **legislation**, ...

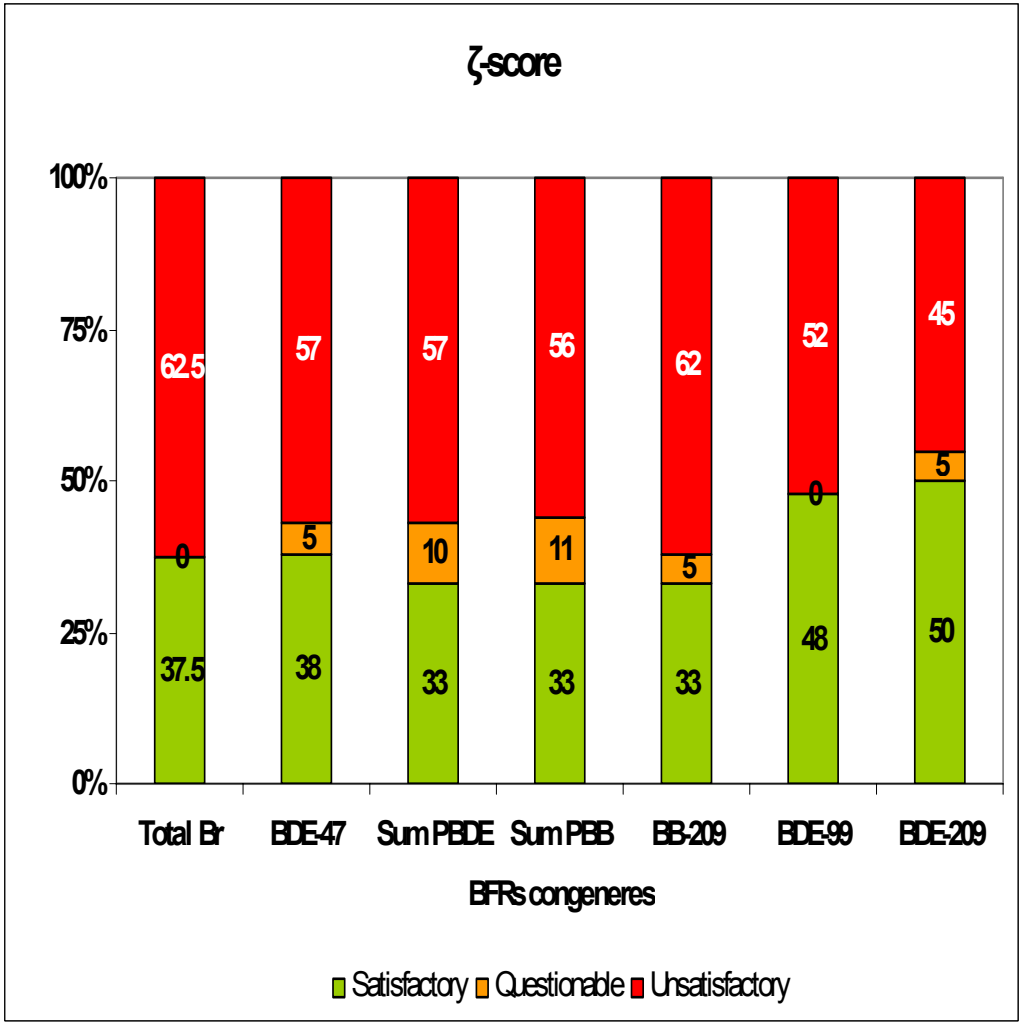
σ = 25 % of X_{ref}

$$zeta = \frac{x_{lab} - x_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}}$$

states if the laboratory result agrees with the assigned value within the respective uncertainties

z- and ζ-Scorings

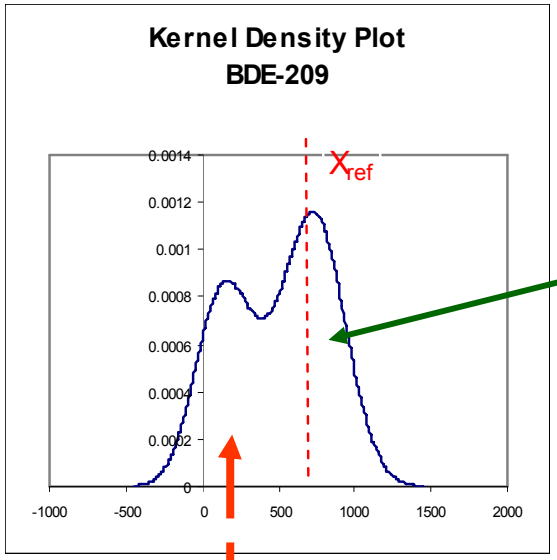


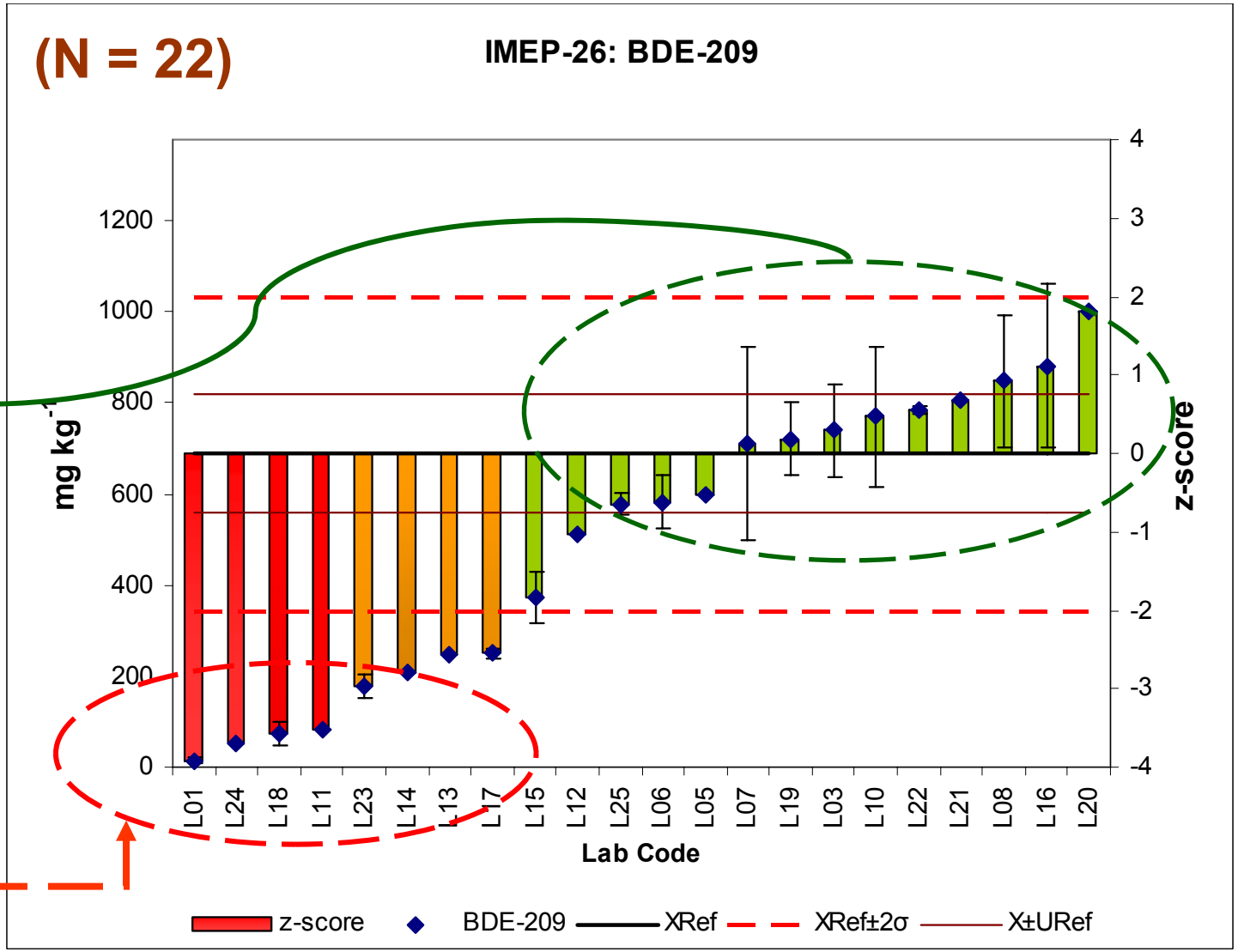


61 - 88 % Satisfactory

Lower ζ-scores

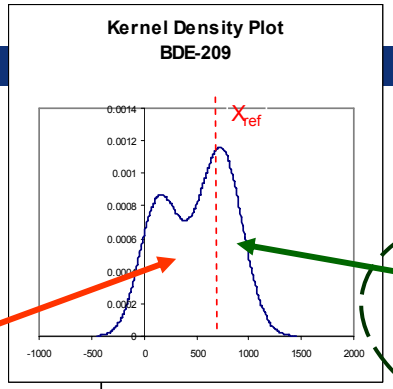
Results: BDE-209

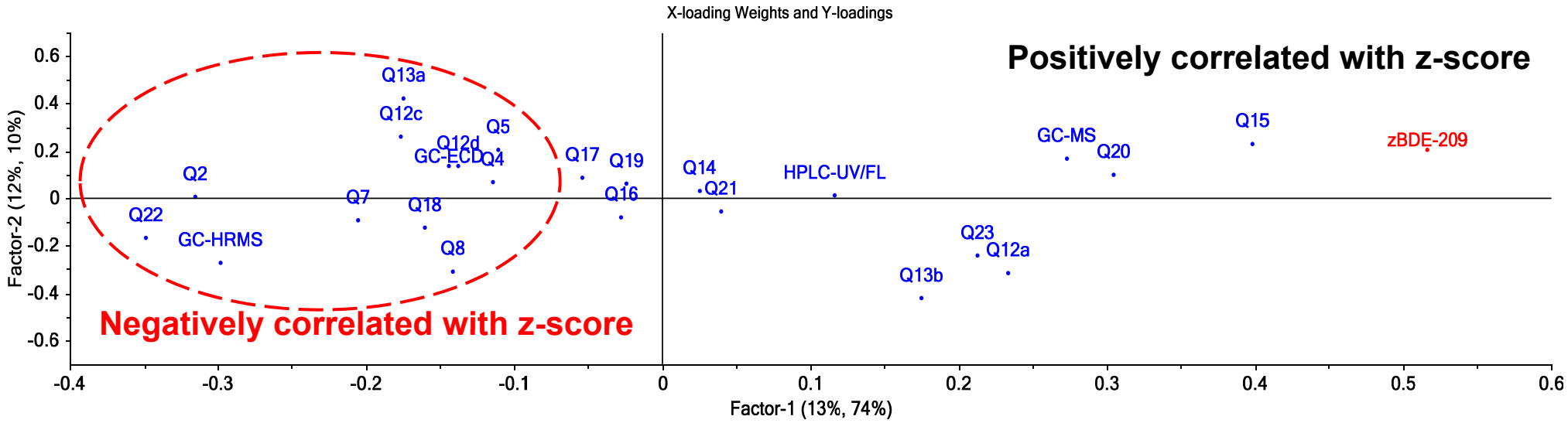




64 % Sat., 18 % Que., 18 % Uns.

BDE-209: PLS-R Models





BDE-209: PLS-R Conclusions

Model "captures" 85 % of total variance

(RMSEC = 0.68, z-BDE209 Std = 1.82)

Positively correlated with z-score (+ accuracy):

Grinding the test samples Q 15

Use instrumental extraction techniques

Soxhlet Q 12a or ultrasonic Q 12c

Carrying out this type of analysis regularly Q 23

Participating in ILCs for this type of analysis Q 20

Use special UV protection Q 16

Use isotopically labelled int. standards Q10

Negatively correlated with z-score (- accuracy):

Use longer GC columns (30m, degradation) Q 07

Opposite to the above

VITO:

- **Isotopically labelled** int. standards **used**
- Test samples were **cryogenically grinded**
- **Soxhlet extraction** used

  (IEC 62321:2008, tBr only, PBB and PBDEs informative, GC-MS)

TÜV Taiwan:

- **Isotopically labelled** int. standards **not used**
- Sample cut into small pieces
- Shaken manually after the addition of organic solvent
- Samples **neither grinded nor underwent Soxhlet extraction**

  (or any other sort of instrumental extraction technique)

Extraction efficiency!

Conclusions

☹ **Compliance with legislation? - Not satisfactory!**

33% reported PBDEs compliant

(< 1g kg^{-1} when X_{ref} = 1.8 g kg^{-1})

☹ **Determination of BFRs needs improvement**

(IEC 62321 Ed.1)

☺ **Appropriate CRMs recommended**

(ERM-EC590, ERM-EC591)

☺ **Multivariate analysis identifies reasons for data bimodality**

(certifier TÜV)