Heavy metals and release in glass containers: a statistical survey 1974-2008

SSV Stazione Sperimentale del Vetro
The Glass Research Centre

MAIN EXPERIENCES AND KNOWLEDGE
Chemical and physical dpt

- Study and characterization of industrial glasses;
- Surface analyses and studies on glass in contact with other materials;
- Environmental analyses;
- Compliance test on glass products (food contact; ROHS; REACH; waste disposals; glass recycling, pharmacopeia, etc.)
- Chemical analyses of glass, raw materials and silicate materials;

MAIN EXPERIENCES AND KNOWLEDGE

thermophysical dpt

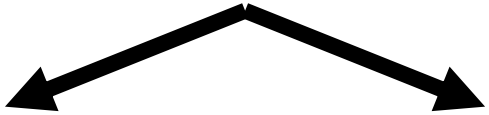
- Refining, bubble analyses, mechanical strength of glass containers, containers lightening
- Finite elements analyses; heat balance, high temperature measurements of glass properties
- Defects and inhomogeneities;
- Mechanical resistance of final products;
- Optical, thermal and energy characterization of glazing and container glass

OUTLINE

- The presentation illustrate the results of a research requested and supported by the Association of Italian Glass Producer.
- It analyzes the release of metals from glass and its correlations with the percentage of cullet reused in the process.
- The aim was to demonstrate that the increase amount of lead in the glass due to the increase of cullet recycled, doesn't imply an increase risk of release of lead in food or environmental matrices.

Legislative Context

Directive 94/62/EC on packaging and packaging waste



Reduction of packaging and packaging waste

Increase of glass recycling
Target 60 % (2006)

Reduction of the concentration of heavy metals in packaging

Maximun amount of
Pb, Cd, Hg, CrVI
100 mg/kg

DEROGATION FOR LEAD

COMMISSION'S DECISION of 19 February 2001

Lead 100 mg/kg	Cadmium 100 mg/kg	Mercury 100 mg/kg	Chromium VI 100 mg/kg
no always respected	respected	respected	respected

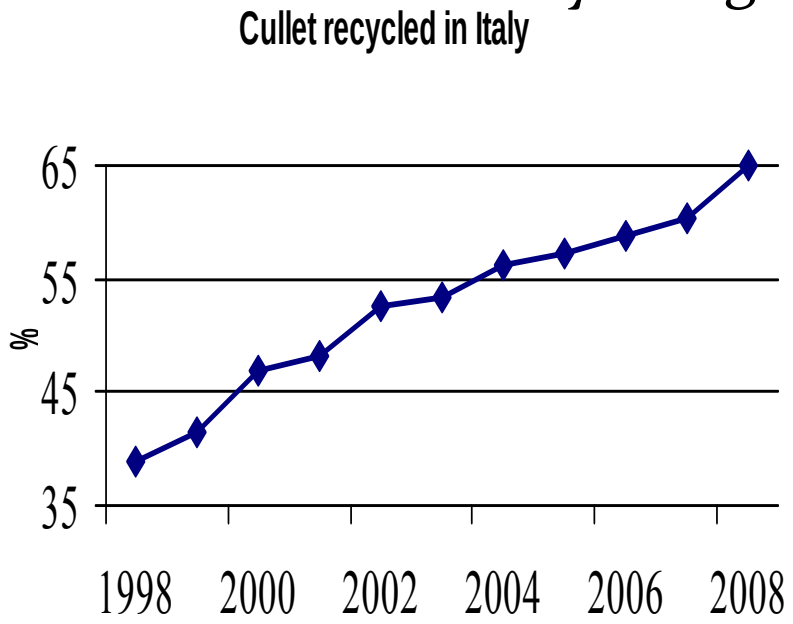
recycled glass is contaminated by glass material containing high quantities of lead

Derogation to 200 mg/kg (average heavy metals conc. levels on any twelve consecutive monthly controls made from the production of each individual glass furnace)

RECYCLED GLASS IN ITALY

Every year, the glass industry increases the use of recycled glass with a lot of positive outcome:

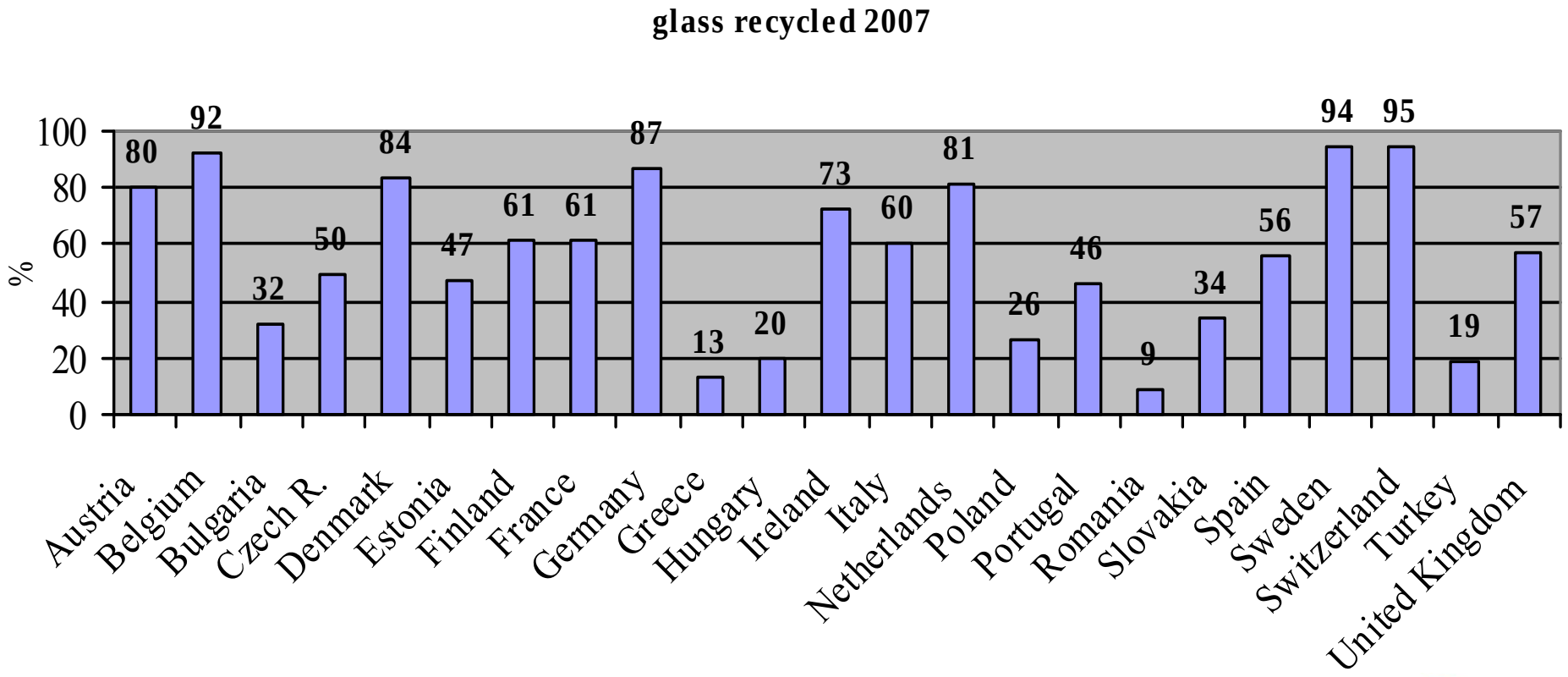
- Reduction of the amount of pollution emitted per tonne of glass manufactured.
- Reduction of energy consumed (every 10 % of cullet used in the batch provides a reduction of 3 % of energy consumption).



The real problem is to find cullet supply in the market (white glass).

RECYCLED GLASS

The percentage of external cullet reused in the batch changes significantly from country to country



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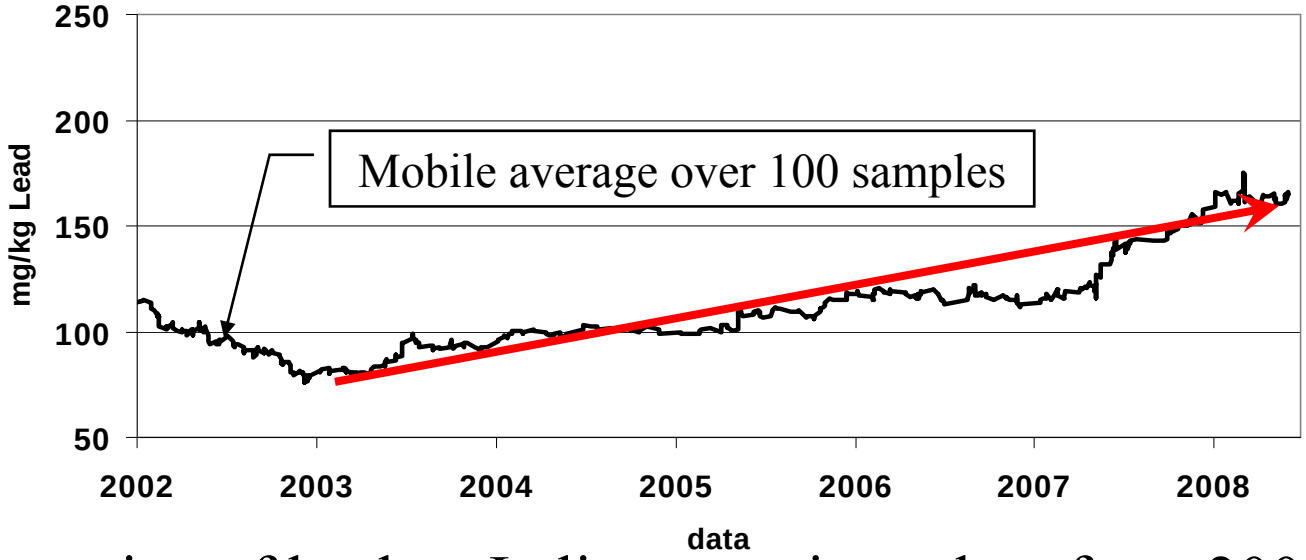
LEAD ON GLASS

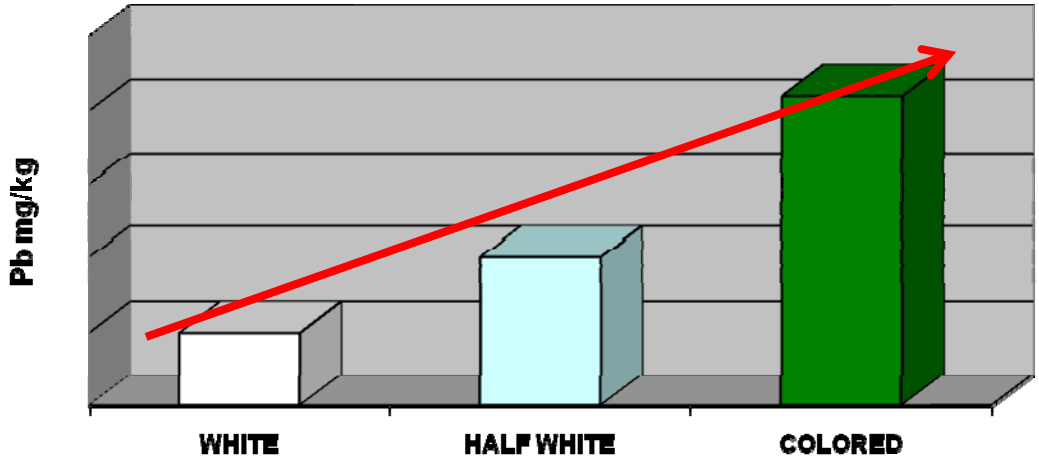
Unfortunately there seems to be a direct correlation between the use of cullet in the glass production and the amount of lead in the glass. Increasing the amount of cullet reused in the process, increases the amount of lead in the glass.



Concentration of lead on Italian container glass from 2002 to 2008 (analysis carried out from SSV – 671 samples) .

CORRELATIONS BETWEEN RATE OF RECICLYNG AND LEAD ON GLASS

The correlations between lead and quantity of glass recycled is particularly evident considering the different colours



Percentage of cullet (%)	20-30	30-50	70-90

FIRST CONCLUSION

The full applications of the level of 200 mg/kg might have as a consequence that the use of recycled glass should be reduced. This result is not desirable, both in terms of enviromental impact than of energy consumpions

QUESTIONS

Has this obligation sense for the glass containers?

The aim of this research was to show that the increased amount of lead in glass doesn't necessarily imply an increased amount of lead released on food or on the environmental matrix

CARATTERISTIC OF INERTNESS OF GLASS

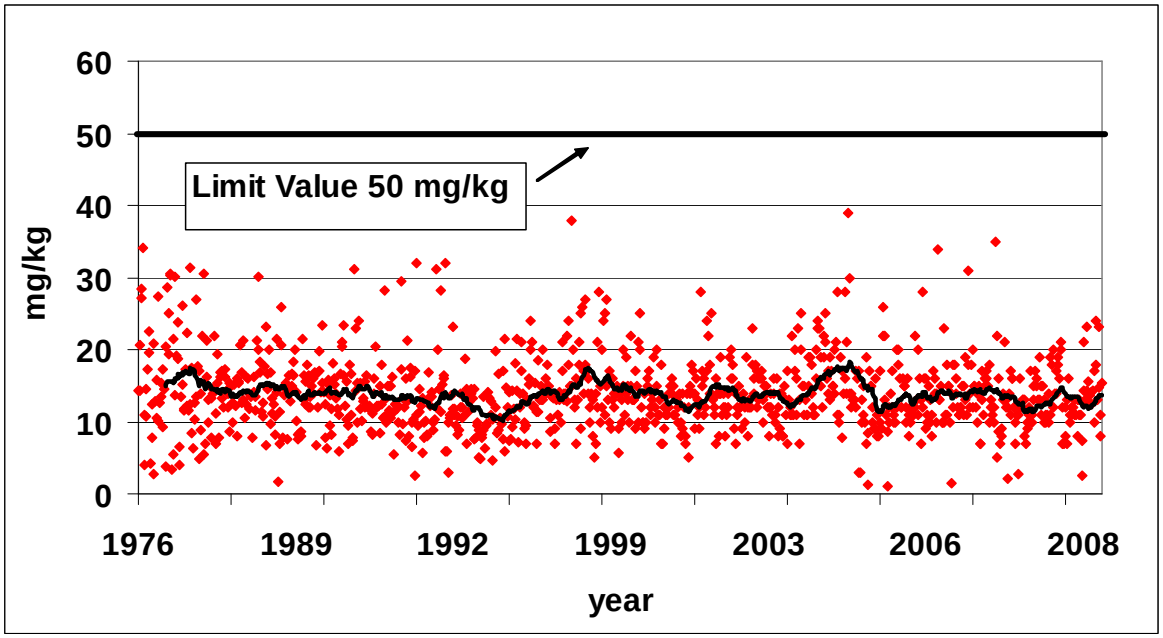
- Glass is chemically inert and has been granted derogations or exemptions in European legislation (Landfill Directive, RoHS Directive…).
- Glass vessels (and most often borosilicate glass vessels) are extensively used in “in vitro” tests, clearly illustrating that glass is one of the most chemically and biologically inert known material
- Glass is extensively used as inert matrice for dangerous substances (inertizzation of dangerous waste, innertizzations of nuclear waste, ecc.)
- Human beings have been in contact with glass (flasks, bottles, jars, drinking glasses, windows…) for thousands of years without any reported adverse effects

FOOD CONTACT
Total Migration

- Specific obligation in Italy (Decrete of Ministery 21 march 1973) for glass containers
- Total migration has to be below
  - 50 mg/kg for containers with capacity above 500 ml
  - 8 mg/dm^2 for containers below 500 ml
- Test carried out on a container filled with distilled water, in autoclave for half an hour at 120 °C. Determination of dry residue after evaporation of the water

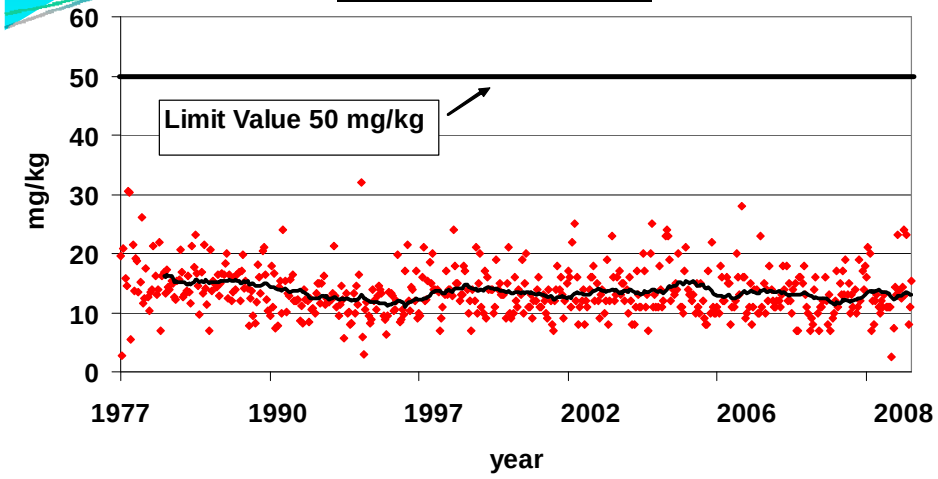
FOOD CONTACT
Total Migration

1343 containers with capacity above 500 ml have been analysed from 1976 to 2008.

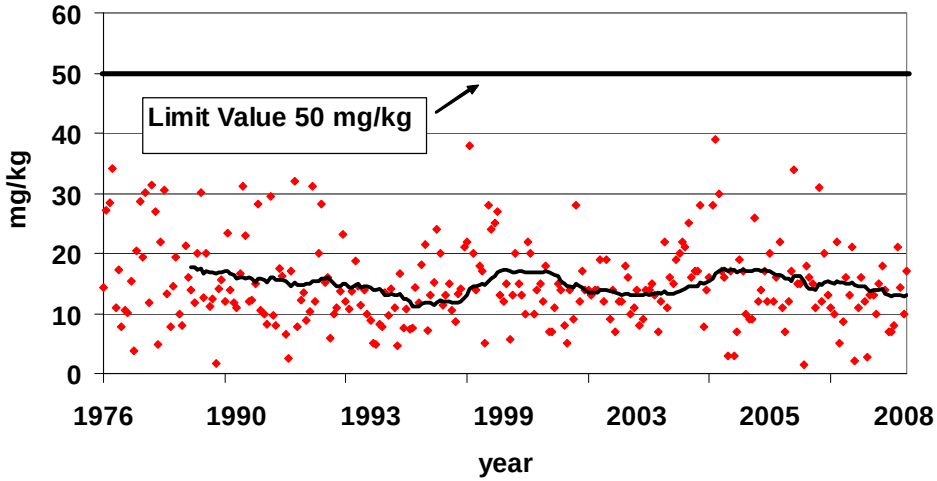


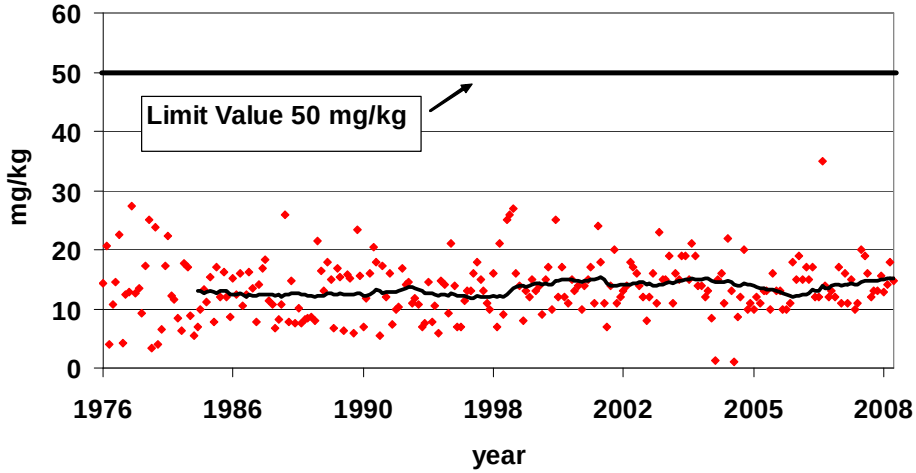
The distribution is homogeneous along the years. Clearly there is no correlations between the amount of cullet reused in the process and the total migrations. The same behaviour can be seen for the differents colors.

Green Glass



White glass





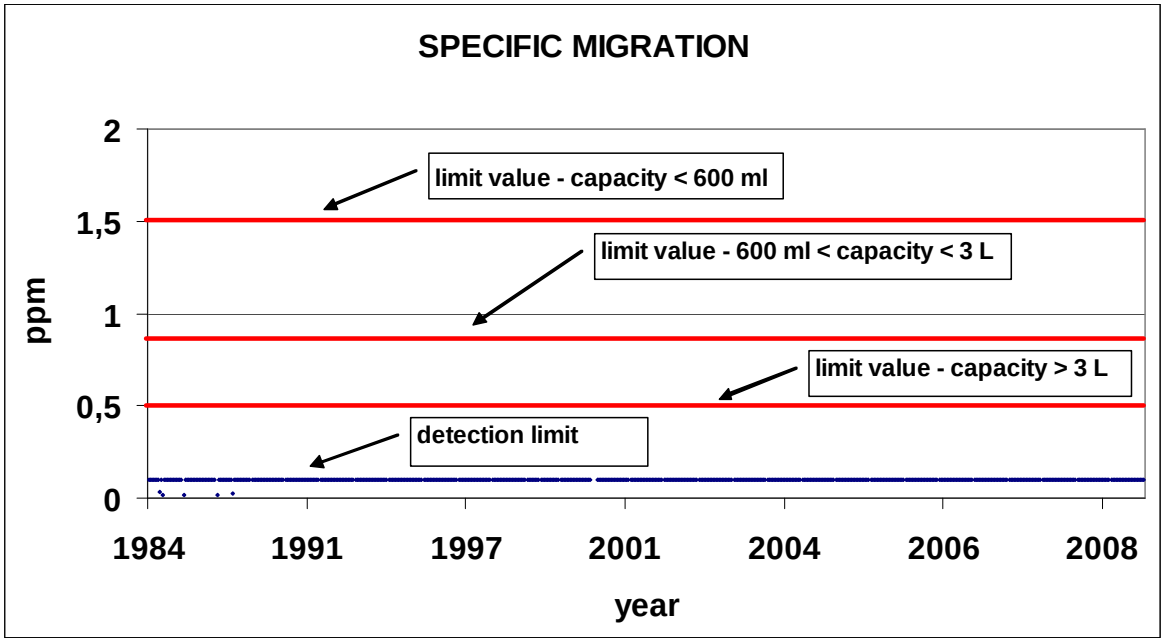
Half White Glass

FOOD CONTACT
specific migration of lead

- No specific obbligation in Italy
- At international level there is a norm to check specific migration: ISO 7086:2000
- Differents limits for differents capacity
  - 1.5 mg/l for containers with capacity < 600 ml
  - 0.75 mg/l for containers with capacity > 600 ml and < 3 l
  - 0.5 mg/l for containers with capacity > 3 l
- Test carried out on 4 containers filled with a solution of acetic acid 4 %, for 24 hours at 20 °C. Determinations of Pb and Cadmium by AAS

FOOD CONTACT
Specific migration

630 containers from 1984 to 2008have been analysed.



The results have been always below the detection limits.
Clearly there is no correlations between the amount of cullet reused in the process and the total migrations.

DISCUSSION OF THE RESULTS

- The containers on the market show a total and specific migration always below the limit values
- There is no correlation between the percentage of cullet reused in the process and the total and specific migration
- The increased use of cullet in the process and, as consequence, the increase of lead in the glass doesn't seem to imply an increase of risk for the consumers

LABORATORY TEST

In order to understand what could happen in the future with higher percentage of cullet reused in the process and probably a higher amount of lead in the glass, some tests have been carried out to investigate the release of metals at higher concentration of lead and using a more sensibile analitical technical device :

- 7 containers of differents colors with a variable concentration of lead between 170 mg/kg and 900 mg/kg
- 1 plate prepared in lab with a concentration of lead of 1200 mg/kg

All the 8 samples were analysed by DRX to pre-determine the amount of lead

Samples tested

Type	Color	Volume (ml)	Concentration Pb (mg/kg)
Bottle	Green	1595	170
Bottle	Green	780	313
Bottle	UVAG	770	331
Bottle	Green	730	457
Big bottle	Half white	5094	870
Small bottle	Half white	109	870
Bottle	Half white	772	900
Plate	Green	-----	1200

Migration test

Each sample was submitted to two different kinds of migration tests:

- 1 or more containers (total volume 1 litre) were filled with distillated water and left in an autoclave for half an hour at 120 °C.
- 4 containers were filled with acetic acid 4 % and left for 24 hours at 20 °C

The eluates were analysed by AAS with furnace graphite (detection limit 2 µg/L)

Migration test with water in autoclave for half an hour at 120 °C

Type	Color	Volume (ml)	Pb glass (mg/kg)	Pb release (µg/L)
Bottle	Green	1595	170	< 2
Bottle	Green	780	313	< 2
Bottle	UVAG	770	331	< 2
Bottle	Green	730	457	< 2
Big bottle	Half white	5094	870	< 2
Small bottle	Half white	109	870	< 2
Bottle	Half white	772	900	< 2
Plate	Green	-----	1200	< 2

Migration test with acetic acid 4 % for 24 hours at 20 °C

Type	Color	Volume (ml)	Pb glass (mg/kg)	Pb release (µg/L)
Bottle	Green	1595	170	< 2
Bottle	Green	780	313	< 2
Bottle	UVAG	770	331	< 2
Bottle	Green	730	457	< 2
Big bottle	Half white	5094	870	< 2
Small bottle	Half white	109	870	4.0
Bottle	Half white	772	900	< 2
Plate	Green	-----	1200	5.5

Evaluation of the intake

- The PTWI Provisional Tolerable Weekly Intake (proposed by FAO/WHO Expert Committe for Food Additives 1993) is 25 µg Pb/kg of body weight.
- Considering a maximun amount of lead in the container of 600 mg/kg, the release is always below the detection limit (< 2 µg/L). Considering a body weight of 60 kg and a average consume of beverage of 6 litres it is possible to calculate the weekly intake.

$$\text{week intake} = \frac{< 2 * 3 * 7}{60} < 0.7 \text{ µg Pb/kg weight, week}$$

It is < 2.8 % of the PTWI (no real risk for the consumer)

Furthermore considering the maximun release obatined (< 5.5 µg/L) with a sample with 1200 mg/kg of lead (not available in the market) the weekly intake is really low < 10 %

Discussion of the results concerning food contact

- The release of the containers submited to migration test in autoclave is always below the detection limit, also with higher concentration
- The release of containers submited to migration test in acid acetic is generally below detection limit. Only the sample with the higher concentration of lead (1200 mg/kg) showed a small release (5.5 µg/L) and that one (4 µg/L) with the biggest contact surface and a concentration of lead of 870 mg/kg
- However with the maximun reuse of cullet expected in the future (80 – 90 %), it is predictable a maximun amount of lead in the glass of about 500 – 600 mg/kg. With this concentration the release is below the detection limit (< 2 µg/L)

Enviromental release

- Soda-lime container glass is considered inert from the Europen Legislations on waste.
- However in order to investigate the possible release of metals in the landfill (end of life) 6 containers were submited to leaching test according to EN 12457:2004-2 (leaching test for waste)
- The samples of glasses were broken, sieved below 4 mm and put in contact with distilled water, using a liquid/solid ratio = 10 l/kg and left in agitation for 24 hours at 20 °C. The eluates were analysed by AAS with graphite furnace

Results on enviromental release

Type	Color	Volume (ml)	Concentration Pb (µg/L)	Release Pb (µg/kg glass)
Bottle	White	770	< 5	< 50
Bottle	Half White	770	< 5	< 50
Bottle	Blu	730	< 5	< 50
Bottle	Amber	750	< 5	< 50
Bottle	UVAG	760	< 5	< 50
Bottle	Green	770	< 5	< 50

The release is below the detection limit

Comparison with C.D.2003/33/EC (waste at landfill)

Color	Release Pb (µg/kg glass)	Limit value for inert waste	Limit value for not dangerous waste
White	< 50	500	10000
Half White	< 50	500	10000
Blu	< 50	500	10000
Amber	< 50	500	10000
UVAG	< 50	500	10000
Green	< 50	500	10000

The release is more than 10 times below the limit value for inert waste, and more than 200 times that one for not dangerous waste

CONCLUSIONS

- The limit of 200 mg/kg of lead is too low to allow an increase of glass recycled
- The increase of lead doesn't imply an increase of risk for the consumer (food contact release not increased) or the enviroment (leaching test not increased)
- It doesn't seem to be a real justification for the 200 mg/kg lead limit value on glass
- A derogation or modification of the legislations is necessary to allow glass industries to improve their enviromental performance

THANK YOU VERY MUCH