



Substitution of diarsenic trioxide in Murano glass

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The story in a nutshell

- Arsenic trioxide (As_2O_3) used to be one of the most important chemical used in Murano Island (Italy) to produce its world-famous artistic glass.
- The substance was included in the Authorisation List in February 2012 with a sunset date on 21 May 2015.
- The glassmakers in the Island (mostly small enterprises and artisans) had to make a difficult decision: to apply for authorisation or to substitute.
- As_2O_3 is not used anymore in the artistic glass production in Murano.
- Any other SVHCs in the authorisation pipeline which may jeopardize artistic glass production in Murano?



Inclusion of As_2O_3 in the authorisation list

Background information on Volumes for use in glass (EU)

Excerpt from Background document for Diarsenic trioxide developed in the context of ECHA's 2nd Recommendation for the inclusion of substances in Annex XIV

Manufacturing and use mass flow of As_2O_3 in the EU

Manufacturing		Use in the EU	
	t/y		t/y
Manufacturing	1500	As ultra pure	30-40
Manufacturing of impure form	320	Chemicals	60
Import	500-	Zinc production	500-600
	600	Glass	100-150
		Total use in EU	690-850
Total	~2400	Export to outside EU	t/y
Disposal as waste	-200	As CCA	70-100
		As As_2O_3	1100-1200
		Total exported	~1200-1300
Net total placed on market	2200	Total	~1900-2150

- Date of inclusion in AL Feb 2012
- Sunset date 21 May 2015



The use of As in Murano artistic Glass

- In Murano Island the artistic glass manufacturing used a large amount of arsenic trioxide and for some articles it was an essential component

As_2O_3 **8000 Kg in 2014**
5000 Kg in 2015

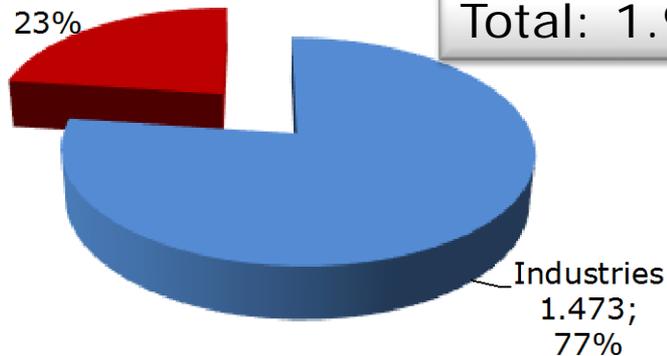
- This oxide was used in the raw material with two main functions:
 - refining agent during the melting process → it helped to remove bubbles (**95% of production volume**)
 - endowing glass with a particular effect → small production of white and opaque glass (**5% of production volume**)



Glass production in Murano area-Year 2015

Glass production volume in 2015 (t/y)

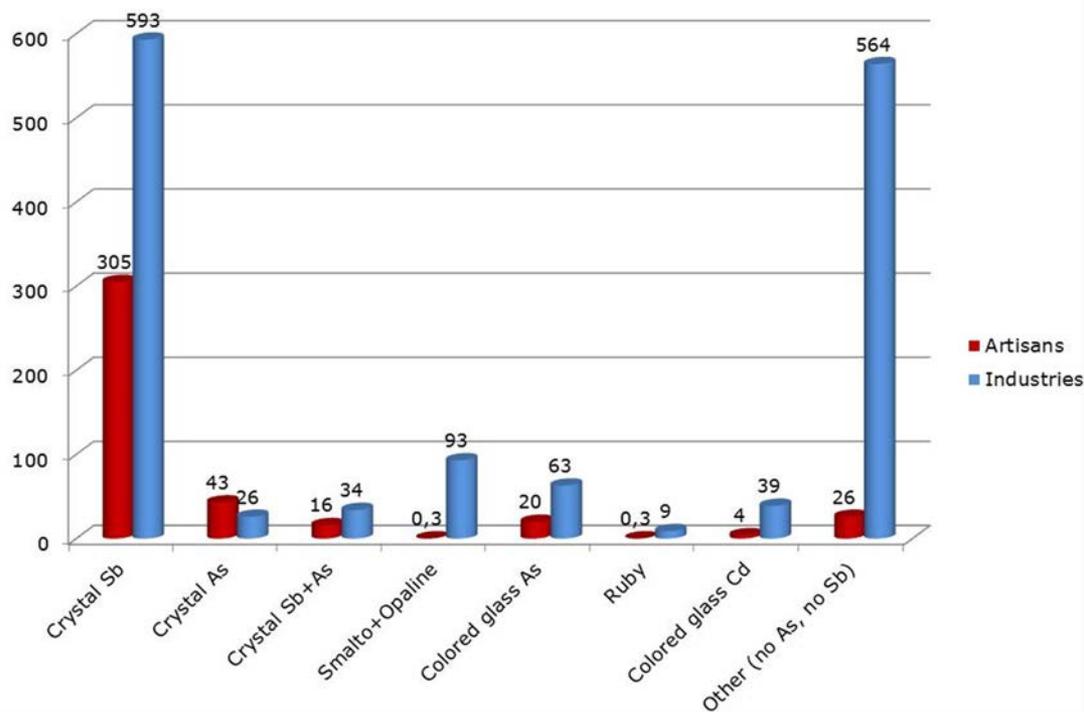
Artisans
435; 23%



Total: 1.908 t/y glass

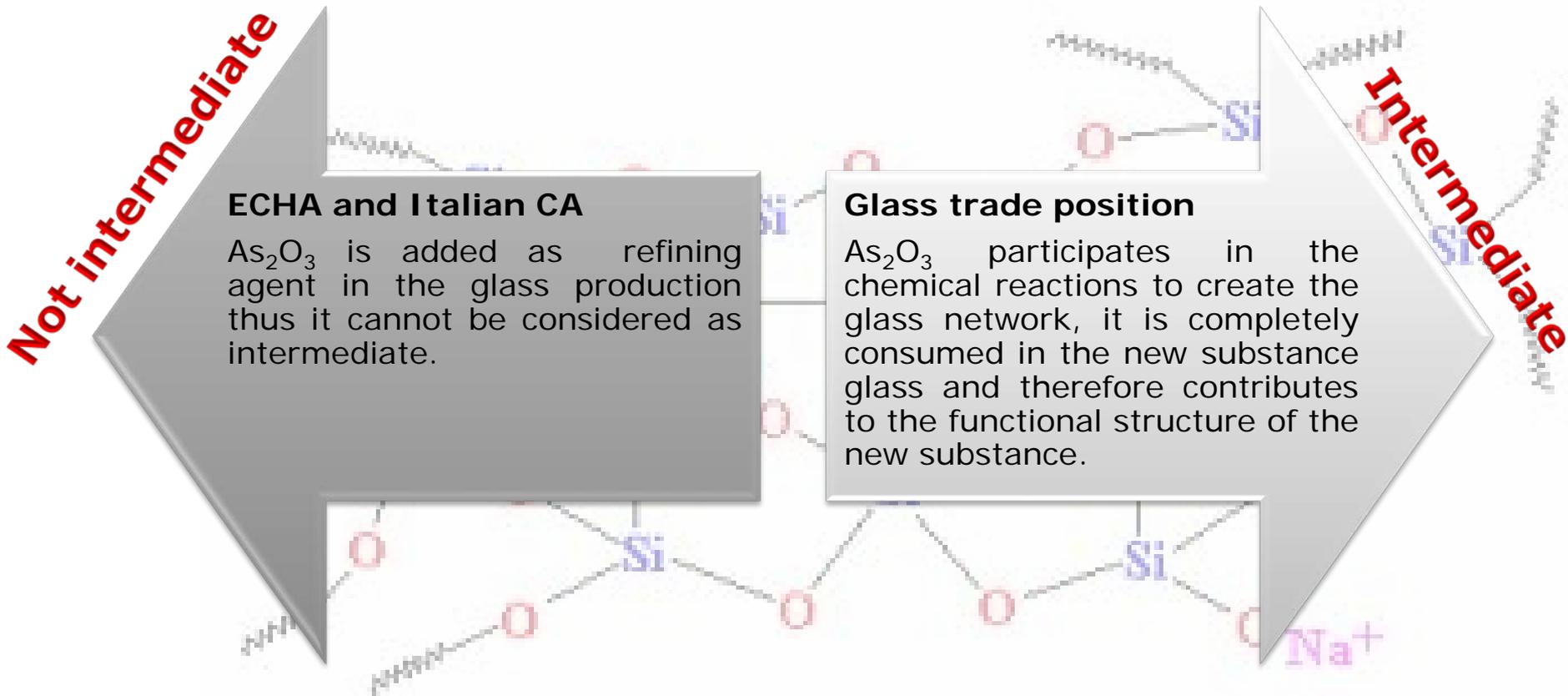
4.869 Kg/y of As
(0.3%)

Annual Production distribution in 35 enterprises-Murano Area (2015)



Intermediate or not?

It was not immediately clear that the glassmakers would need to replace arsenic trioxide as they felt that the substance was being fully consumed during the chemical processing

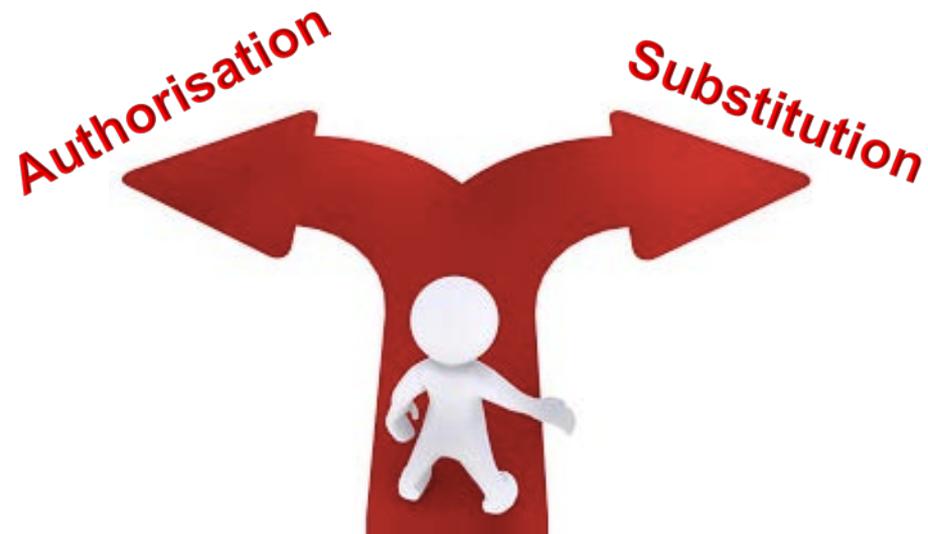


To apply or not to apply

The glassmakers had to make a difficult decision: to apply for authorisation or to substitute

Key elements

- Most of the furnaces are small scale and not big enough to justify the costs of requesting an authorisation for such a specific use.
- Too difficult to apply the technical requirements for achieving an authorisation to the traditional processes in place for producing artistic glass.



In the end

- glassmakers opted to substitute the substance
- no AfA was submitted



Changing mindset...towards substitution

- Dialogue between different parties initiated and promoted by Authorities
- Government-funded research (264.000 euros) undertaken to replace arsenic trioxide by less toxic substances to humans and the environment (including a risk analysis for workers' health)

Two substitutes identified (May 2012)

- Cerium dioxide
- Ground Granulated Blast furnace Slag (GGBS)

but.....

alternative process agents performances do not fully meet the expectations

- they work well at 1500°C instead of 1300-1400°C
→longer melt cycle and more energy required
- changing purification plants→big investments
- lower quality of glass

Substitution



The local enforcement authority activities

After the inclusion of As_2O_3 in Annex XIV

- A capillary informative campaign was initiated (with target glass makers)
- All glass producers were invited to fill in a detailed questionnaire on the processes applied, including information about As_2O_3 (i.e. their specific use, quantity in use and stored).
- From December 2015 an enforcement campaign is being carried out with target artistic glass production sites in Murano and in mainland.

300 questionnaires distributed

114 companies are operating in artistic glass sector

41 companies are melting raw materials

19 companies declared use of As_2O_3 in 2014

Majority of 41 companies declared the substitution of As_2O_3 with a mixture of antimony trioxides, nitrate or carbonate of alkaline metals



Where As_2O_3 is irreplaceable

As_2O_3 Colouring agent in a production niche

Glass	As_2O_3 quantity per 100 Kg sand
Yellow	0-1.0 Kg
Red	0-1.0 Kg
Amethyst	0.4-1.0 Kg
Green	0-1.0 Kg
Smoke	0.2-1.0 Kg
Acquamarine	0.2-1.0 Kg
Opaline	5.0-10.0 Kg
Opala	20.0-30.0 Kg
Silk	2.0-5.0 Kg
Crystal	0-1.0 Kg

A substitution study for the glass "opala" does not exist (only 5% production volume)



Reticello



filigrana

Where As_2O_3 is irreplaceable

Millefiori



New recipe without As

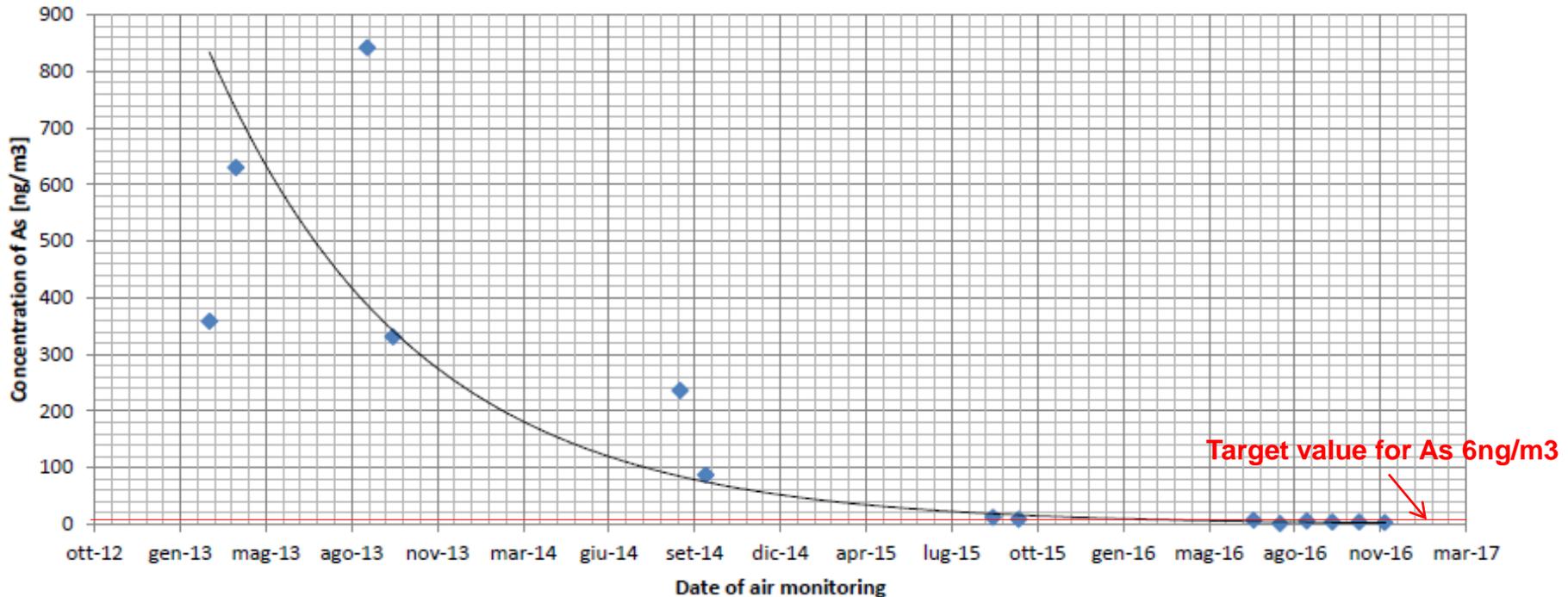
Traditional recipe with As



Zanfirico



Environmental impact: improved air quality



- After the ban of As_2O_3 the concentration of As in island air fell under the target limit value of 6 ng/m³
- Sinergies between REACH and environmental legislation → air quality management in Venice lagune found in REACH a powerful tool
- Environmental monitoring (As and other metals) is still ongoing



Replacement As_2O_3 : facts and impact

- Alternative refining agents are being used in artistic glass production (mix of antimony trioxides, nitrate or carbonate of alkaline metals).
- Some companies stopped the productions for which As_2O_3 cannot be replaced → **5% production volumes correspond to - 23% of turnover.**
- Increased energy consumption (**+20% costs to reach higher temperatures in melting raw materials**).
- Increased costs of R&D for alternatives (small and micro enterprises).
- A clear picture of losses is not available: high variability of data due to different production capacity, type, market.
- Decreased competitiveness of Murano artistic glass in international trade (the use of As_2O_3 is permitted outside EU).



Conclusions and future challenges

REACH as an incentive
innovation while protecting health and environment

- The inclusion of As_2O_3 into authorisation list forced Murano glass makers to find a safer alternative, while trying to maintain the quality of their glassware.
- Impact of authorisation on artistic glass sector seems to be limited to a production niche.
- The case of As_2O_3 represents a good example of joint efforts for substitution.
- Substitution of As_2O_3 has resulted in tangible benefits in air quality.

Future challenges....other SVHCs used in glass production

- E.g. Cadmium sulphide is used for **red** and **yellow** glass production. It is an essential ingredient for these productions and the substitution would heavily compromise the artistic glass sector.



Thank you
and thanks to



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