ASSESSMENT OF CONSTITUENT AVAILABILITY OF SAMPLES OF SPECIAL GLASS WITH REGARD TO THE EUROPEAN REACH REGULATION.

A briefing paper by TC13 - The International Commission on Glass' Technical Committee on the Environment.

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Abstract
The TC13 (Environment) of the International Commission on Glass (ICG) conducted a round-robin analysis of constituent leachability from samples of special glass provided by Schott AG. Sample preparation followed the method developed by TC13 and based on the European Standard EN12457-2 [reference 1]. Leachability results were compared with the landfill criteria in European Council Decision 2003/33/EC [2]. Three special glasses were assessed by the ten laboratories involved. For one glass, the leachability of the lead component, Pb, was evidently higher than the criteria for landfill as non-hazardous waste, and is thus "*available*" during the lifecycle of the glass with regard the REACH regulation [3]. Following the guidelines developed by TC13 [4,5,6], this means that this glass is not exempt from registration and assessment under the European REACH regulation. By demonstrating that the Pb component is available and thus the manufacturer, Schott AG, should register this glass, this study has also shown that TC13's constituent availability assessment, based on the criteria of the landfill test, should be considered an appropriate method to determine whether a glass should be exempt from REACH registration.

Introduction
This practical study was conducted by members of TC13 to support work, primarily led by GAE[1], on the exemption of most glass types from the European REACH regulation. Glass will be exempt if it does not contain any constituents that meet the criteria as dangerous in accordance with Directive 67/548/EC. However, also, "g*lass is exempted if conclusive scientific experimental data show that its constituents, meeting the criteria as dangerous in accordance with Directive 67/548/EEC in concentrations above the lowest of the applicable concentration limits set out in Directive 1999/45/EC or set out in Annex 1 to Directive 67/548/EEC, are not available throughout the life-cycle of the substance.*"

This work follows a study by TC13 to develop a suitable test for proving whether certain constituents "*are not available throughout the life-cycle of the substance"*. [4,5,6] The test that TC13 proposes is based on existing EC methodology and legislation: the standard method EN-12457-2 and the landfill criteria in Council Decision 2003/33/EC (TC13, 2009).

The test procedure EN 12457-2 was chosen by TC13 because it reflects a worse case scenario. It is applied to size-reduced material and the liquid to solid ratio (L/S) of 10 l/kg that is used to elute the sample to reflect the release over a relevantly long time frame [7]. The landfill regulation was chosen as an indicator of whether a substance is

[1] GAE is Glass Alliance Europe, the cross-sectoral association of the European glass industry. www.glassallianceeurope.eu

significantly "*available"* because it is part of an already-established piece of European legislation. "Available" in this case means that a substance could be released from the glass at any time during its lifecycle, including disposal and is thus a worse-case scenario.

The first paper [4] introduced the TC13 method, while assessing the leachability of samples of tableware and cooker top glass. Subsequent studies [5,6] assessed antimony leaching from rolled plate flat glass and selenium leaching from dark tinted flat glass and confirmed the applicability of the methodology, although both glasses passed the test for exemption. (TC13, 2010a and 2010b)

Following the flat glass work, this study focuses on the Special Glass industry. Many special glasses have no constituents "*meeting the criteria as dangerous*" and would automatically be exempt from REACH registration. However, some special glasses do contain such components; for example optical glass often contains heavy metals such as lead, Pb. Although the content of Pb in the glass in some of these products is below the *"lowest of the applicable concentration limits set out in Directive 1999/45/EC, or the concentration limit set out in Annex 1 to Directive 67/548/EC"*, some have concentrations above this level. TC13 thus considered that it would be useful to study these types of special glass compositions.

Samples of three types of special glass manufactured by the German company Schott AG were assessed. Glasses A and B were optical glasses and glass C was another type of technical glass. The significant components of the glasses are shown below. It is important to note that glass itself is a single amorphous homogenous substance and as such the glass samples tested did not contain the individual oxide compounds (like PbO) as such. The contents of the elements of interest are presented in mass % oxides for convenience only. This is a common notation in the glass industry, despite the fact that the individual oxides are not present in the glass substance.

Glass A
Arsenic trioxide (As_2O_3) 0.4%
Lead oxide (PbO) 75%

Glass B
Arsenic trioxide (As_2O_3) 0.2%
Lead oxide (PbO) 45%

Glass C
Boron oxide (B_2O_3) 25%
Lead oxide (PbO) 75%

Method

As noted above, the assessment method followed is described in EN 12457-2. However, the EN12457-2 general procedure requires that *"on no account shall the material be finely ground"*. This poses a problem, because unlike most materials when glass is crushed very fine fragments are unavoidably formed. The previous TC13 papers (2009, 2010a, 2010b) addressed this issue and recommended that the method be slightly modified by removing (sieving) fragments smaller than 0.5mm.

To further refine this study, and remove any laboratory-to-laboratory variation of the sample preparation process, Schott provided samples of their glasses to Stazione Sperimentale del Vetro (SSV) in Italy who then prepared the crushed and sieved samples for the round robin assessment.

Elution and analysis of replicate samples of the glass prepared by SSV was conducted by the following laboratories:

- NSG Pilkington – England
- SSV – Italy
- St. Gobain – Germany
- Şişecam – Turkey
- British Glass – England
- Schott AG – Germany
- Guardian – USA
- ARC International - France
- INISMa - Belgium
- Saint Gobain Research - France

The samples were all provided by SSV, so there was no variability introduced by the preparation process. The samples were prepared in the following way:

- crushing by manual hammering;
- sieving to produce a size range between 4 and 0.5 mm (TC13 methodology);
- delivery to labs of 300 g of each sample by courier.

The laboratories employed elution equipment prescribed in the EN 12457-2 method. Chemical analysis equipment is not prescribed and the laboratories used different techniques: graphite furnace atomic absorption spectroscopy (gAAS); hydride generation atomic absorption spectroscopy (hAAS); inductively-coupled plasma optical emission spectroscopy (ICP-OES); and inductively-coupled plasma mass spectroscopy (ICP-MS). These techniques have different detection limits.

Results and discussion

The laboratories analysed for a range of elements, including As, Cd, Cr, Pb, Sb and Se. The Cd, Cr and Sb concentration in the eluates was below the detection limit of the equipment of any of the laboratories. This was not unexpected, because the glasses did not contain any of these elements.

For arsenic, As, some laboratories measured a concentration just above the detection limit of their equipment, but for others the concentration of any As present was below the detection limit. Because the detection limits of the laboratories' equipment varied it was impossible to calculate an average value in the eluate. However in all cases the concentrations were below the European limit for landfill as non-hazardous waste. This value in Council Decision 2003/33/EC relating to criteria for acceptance to landfill as non-hazardous waste is 2.0 mg/kg of As.

For lead, Pb, the results are more interesting and for one sample, a different conclusion is reached. For, Pb, the average concentration measured in the eluate indicated that following amounts leached from the glass samples:

Glass A: average 5.38 mg/kg (Std.dev. 4.02 mg/kg, CV 74.6 %)
Glass B: average 7.96 mg/kg (Std.dev. 5.09 mg/kg, CV 74.1 %)
Glass C: average 12463 mg/kg (Std.dev. 1796 mg/kg, CV 14 %)

Some lead was detected in the eluate from glass A (5.38 mg/kg) and glass B (7.96 mg/kg). Note that for glass B one laboratory reported a value of lead below the detection limit (0.1 mg/kg), but as this was considered an outlier it was not used in the calculation. For both samples A and B, the average value was below the limit value of 10 mg/kg Pb in Council Decision 2003/33/EC relating to criteria for acceptance to landfill as non-hazardous waste. As such the Pb, like the other components of interest should be considered as "*not available*" and these glasses are exempted from registration. However it should be noted that for sample B the average value plus the standard deviation was above the limit, indicating there was some uncertainty in the result and that the glass should be re-tested.

The much higher value of 12463 mg/kg clearly indicates that the Pb in glass C would be "*available throughout its life-cycle*" as it leached into the eluate solution and resulted in a concentration far greater than the non-hazardous waste landfill criteria. As such, this glass could not be sent to non-hazardous landfill, and importantly it cannot be exempt from REACH registration. The glass producing companies for this type of glass are thus required to register this glass and ensure that its use is properly authorised.

Conclusions

The results of this study demonstrate that the elution test developed by TC13 and based on the criteria of the landfill directive is an acceptable method to identify whether components of the glass are "*available throughout its life-cycle"* and thus whether a glass could be eligible for exemption from REACH. One type of technical glass assessed in this study did not pass the eligibility criteria for landfill as non-hazardous waste and as such would have to be registered for authorised use according to the REACH directive.

References

[1] EN 12543-2 Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction).

[2] Council Decision 2003/33/EC. Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC.

[3] Council Decision 1907/2006/EC establishing REACH and ECHA.

[4] TC13 2009. Preliminary report on a method to determine the availability of glass constituents with regard to the European regulation REACH. This will be available on the TC13 part of the ICG website www.icglass.org

[5] TC13 2010a. Assessment of constituent availability of antimony-containing rolled plate glass with regard to the European REACH regulation. A briefing paper by TC13 - The International Commission on Glass' Technical Committee on the Environment. Issued January 2010. This will be available on the TC13 part of the ICG website www.icglass.org

[6] TC13 2010b. Assessment of constituent availability of selenium-containing float glass with regard to the European REACH regulation. A briefing paper by TC13 - The International Commission on Glass' Technical Committee on the Environment. Issued August 2010. This will be available on the TC13 part of the ICG website www.icglass.org

[7] Hans van der Sloot, Joris Dijkstra, Ole Hjelmar, Gerd Spanka, Philo Bluyssen and Sara Giselsson. Evaluation of a horizontal approach to assess the possible release of dangerous substances from construction products in support of requirements from the construction products directive (tr2). Förderkennzeichen (UFOPLAN) 206 95 384. November 2008.

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