Wet chemical analysis of the redox state of glass

Germany's Institut für Glas- und Rohstofftechnologie (IGR) was founded in January 2008 and has developed to become an efficient service provider to the glass industry. Here, IGR* gives an overview of its work, focusing on Fe^{2+} analysis.

As an independent and neutral institute, IGR carries out physical and chemical analysis on glass and raw materials, as well as on waste glass from glass recycling.

Another focus of activity is on analysis in the identification and fraction analysis of glass splinters.

IGR operates as a consultant to renowned glass melting factories, raw material suppliers and glass recycling companies advising on batch, melting, and moulds process as well as cooling, and hot and cold coating issues through the entire technology chain. In addition, its consultants advise on production optimisation and overcoming defects.

IGR prides itself on its research and development, internal and external training programmes and laboratories. The institute uses an IGR internal Quality-Management-System that complies with DIN EN ISO/IEC 17025. Additionally, IGR analyses construction materials and fire retardant materials as well as examining harmful materials such as asbestos or mineral fibres.

Founded in 2008, IGR won the Göttingen, Germany innovation award in 2010, 2011 and 2013. It has 10 employees and its analytical services include:

REM-EDX for inclusions, cords, particles, asbestos and mineral fibres; ICP-OES for chemical analysis from glass, raw material and heavy metals (50 elements, included B); FTIR for synthetic material and oil analysis; OH in glass,

detection from Cold end coating and varnishing.

Other services include specific glass analysis (glass fracture, seeds, blisters, strains, homogeneity,density, inclusions, several corrosion tests, migration, splinters identification,several stability verification and laboratory glass melting). The institute also samples analysis from heterogeneous glass recycling waste, among other things, to assess the quality from recycled glass.

Wet-chemical analysis

In recent years, there has been considerable demand at IGR for reproduceable Fe^{2+} analysis in silicate material from the glass manufacturing industry.

The negative environmental impact on the analysis is a well-known problem.

A possible methodology has been suggested by DIN EN ISO 14719, entitled 'chemical analysis for non-flammable material, glass and varnishes – the spectral – photometer determination from Fe^{2+} and Fe^{3+} with 1.10-phenanthroline (ISO 14719:2011); German edition EN ISO 14719:2011'.

However, current research using this methodology, including those of S. Bartolomey, (Aachen, Germany), has proved inconclusive.

Since the beginning of 2013, IGR has worked on the practical implementation of the Fe^{2+} analysis in silicate raw and basic materials. Initially it undertook extensive literature reviews, most notably articles written by P. Brosch and H. Hahn (1992) and those detailing the ICG method (1999).

Following this, the IGR spent several months working on the practical implementation of the Fe^{2+} analysis, and on defining a methodology based on the Norm. The resulting analysis is robust and free from negative environmental factors (such as UV radiation, shielding gas application), as well as interference by polyvalent elements in the glass matrix.

Table 1 lists the wet chemical Fe^{2+} analysis in accordance with the IGR method of various soda-lime glasses (KNG) and borosilicate glass (Boro).

The 5th column shows the traditional Fe^{2+} values, taken using conventional transmission measurements. These can be directly compared with the results of the wet chemical Fe^{2+} analysis in column 3, gained using the IGR method. In addition to the expected variations in the

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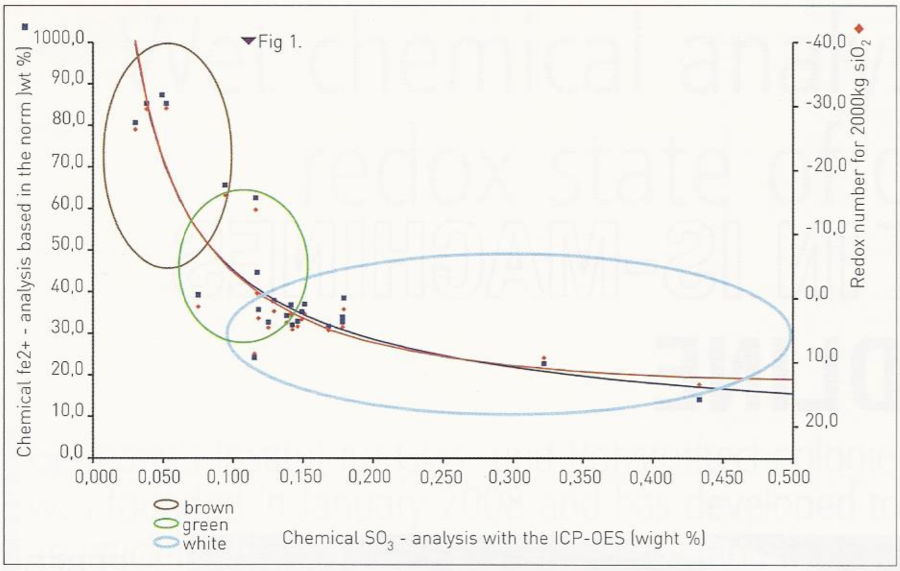

results for coloured glass, there were also large differences recorded for white glass. Furthermore, column 6 of the table includes the redox numbers (RZ), calculated using the chemical Fe^{2+} analysis in accordance with the IGR method, based upon the findings of M. Nix and HP Williams (1990) for 2000kg SiO_2.

Column 4 sets out for comparison, an internal IGR Fe^{2+} model, resulting from various calculations of transmission values for UV-VIS analysis and several chemical parameters from the ICP-OES analysis.

Further analysis of the Fe^{2+} results that were determined by the wet-chemical IGR reproducible method are listed in ***Fig 1***. The dependencies can be seen between the ICP - OES values with the corresponding SO_3 concentrations.

The graph also shows the corresponding redox numbers to the respective SO_3 concentrations. It shows not only the results for the typical white, green and brown soda-lime glass, but also the foliage coloured and highly reduced white glass.

Thus for example, the graph shows that a green glass with a Fe^{2+} score of 36wt%, which was determined using the wet-chemical IGR method, has a corresponding redox number of +2.

In particular, this graph devised by the IGR shows the reproducible correlation of the three individual parameters Fe^{2+} - SO_3 - RZ as well as the overlapping of the corresponding curves.

In conclusion, the IGR method to determine the wet chemical Fe^{2+} analysis is reproducible, largely free from negative influences, and can lead to big improvements in the assessment of the redox state of glass melting units.

These include:

- Detection of the redox potential
- Earlier detection of unwanted glass staining
- Control of Fe^{2+} concentration
- Economy of energy and raw material supplies
- Reduction of necessary decolorising
- Detection of colour cords in brown glass ■

Sources

1 DIN EN ISO/IEC 17025, Allgemeine Anforderungen an die Kompetenz von Prüf- und Kalibrierlaboratorien, (ISO/IEC 17025:2005); German and English version EN ISO/IEC 17025:2005

2 DIN ISO 14719, Chemische Analyse von feuerfestem Werkstoff, Glas und Glasuren – Spektralphotometrische Bestimmung von Fe^{2+} und Fe^{3+} mit 1,10-Phenanthrolin (ISO 14719:2011); Deutsche Fassung EN ISO 14719:2011

3 P. Brosch/H. Hahn (1992), Kolorimetrische Bestimmung von Fe(II) und Gesamteisen in Silikat- und Boratglas, WW III – Analytische Labor – 1-2"
Institut für Werkstoffwissenschaften (Glas und Keramik) Erlangen - Nürnberg

4 ICG Verfahren, Glass Technology 40,1999, No. 1, 24-28

5 M. Nix/H. P. Williams (1990), Glastechnische Berichte 63K S.271-279
Calculation of the redox number of glass batches containing recycled cullet

6 Bamford/Hudson, ilis GmbH, Spektralanalyse und Farbmessung in der Glasindustrie Mai 2002 S.50

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		Fe²⁺ (%)			Redoxnumber (RZ)
Glass	glass - smelter	wet chemical analysis from IGR based in the norm DIN EN ISO 14719 source: [2]	modelled calculation from the transmission and the ICP	transmission after Bamford/Hudson Source: [6]	RZ 2000kg SiO_2
KNG white	GS1	22,7	23,5	24,5	9,3
KNG eco white	GS2	34,3	33,5	25,4	3,8
KNG white - by waste glass reduced in coal-yellow	GS2	65,6	64,5	26,3	-16,1
KNG white- by waste glass reduced in green	GS3	62,5	57,3	32,1	-13,8
KNG green	GS4	24,1	22,2	17,9	8,7
KNG brown	GS5	80,7	78,2	5,3	-26,4
Boro 3.3 white	GS6	30,8	27,8	7,6	5,9

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