Original Paper

Investigations into the existence of hexavalent chromium in industrial glasses

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In several melting experiments the existence of hexavalent chromium in soda–lime–silica glasses depending on the oxidation conditions and the presence of iron have been investigated by means of a recently proposed wet chemical analysis procedure. The observed dependence of the concentration of hexavalent chromium on the iron content can be explained by means of an electron exchange between iron and chromium during cooling. The results have been applied to the conditions of industrial glass melting. Under sufficiently reducing conditions and high portions of iron the existence of hexavalent chromium can be excluded. These conditions are fulfilled for all commercial container glasses investigated.

Untersuchungen zur Existenz von sechswertigem Chrom in industriellen Gläsern

In einer Reihe von Schmelzversuchen wurde das Vorhandensein von sechswertigem Chrom in Kalk-Natronsilicatgläsern mit einem kürzlich vorgeschlagenen naßchemischen Analyseverfahren in Abhängigkeit vom Oxidationszustand und vom Eisengehalt der Gläser untersucht. Die beobachtete Abhängigkeit der Konzentration an sechswertigem Chrom vom Eisengehalt kann mit dem Austausch von Elektronen zwischen Eisen und Chrom beim Abkühlen erklärt werden. Die Ergebnisse wurden auf die industriellen Glasschmelzbedingungen übertragen. Unter ausreichend reduzierenden Bedingungen und bei genügend hohem Eisengehalt kann das Vorhandensein von sechswertigem Chrom ausgeschlossen werden. Diese Randbedingungen waren für alle untersuchten handelsüblichen Behältergläser erfüllt.

1. Introduction

Chromium is a very important coloring agent in the container glass industry. In the trivalent state it provides the green color which is used in green and dead leaf green glasses. Besides the trivalent state also hexavalent chromium can exist in oxidized glasses. Hexavalent chromium is known to be very toxic, thus, there is a strong interest to avoid this particular chromium species in container glass.

Additionally, in 1994 the directive 94/62 on packaging and packaging waste of the European Commission was introduced [1]. According to that directive the sum of concentrations of lead, cadmium, mercury and hexavalent chromium in packaging material is subject to a decreasing limit of 600 ppm by weight from two years after enacting, 250 ppm from three after enacting and 100 ppm from five years after enacting the directive. Cr^{6+} seems to be of minor concern in industrial chromium-colored glasses [2]. However, from UV-absorbing green glass it is known that under certain conditions considerable quantities of Cr^{6+} can exist. The directive 94/62 restricts the sum of mercury, cadmium, lead and Cr^{6+}. In this situation, it is very disadvantageous that the analytical methods of the quantitative Cr^{6+} determination are still being discussed.

In order to avoid any problem concerning hexavalent chromium, this paper investigates how the generation of Cr^{6+} can be excluded by chosing appropriate boundary conditions. The generation of Cr^{6+} can be suppressed by adding either reducing agents or iron. Several melting experiments have been carried out in order to determine quantitatively the conditions for a reliable Cr^{6+} suppression. For a reliable quantitative Cr^{6+} detection a new wet chemical method has been tested. The results are discussed from a thermodynamic point of view, and a recommendation is given in order to avoid the development of Cr^{6+} in the industrial glass melting process.

2. Redox behavior of chromium and iron in glass melts and glasses

In soda–lime–silica glass four oxidation states have been reported for chromium. The most important species is Cr^{3+} [3 and 4], which is widely used to produce green and dead leaf green glasses. Besides Cr^{3+} also glasses containing Cr^{2+} [5], Cr^{5+} [6 and 7] and Cr^{6+}

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[3, 4 and 8] have been reported. In oxidized glasses Cr^{2+} and Cr^{5+} exist only in negligible amounts, thus, the oxidation reaction of chromium can be written

$$Cr^{3+} + \frac{3}{4} O_2 \rightleftarrows Cr^{6+} + \frac{3}{2} O^{2-}. \quad (1)$$

The respective oxidation states exist in different coordinations with respect to the free oxygen ions. This causes a dependence of the oxidation state not only on the oxygen partial pressure, but also on the basicity of the melt. However, because of the buffering action of the non-bridging oxygen ions, the basicity can be assumed to be constant with respect to the oxidation reaction of iron and chromium if the total concentration of the respective polyvalent element is sufficiently small. Thus, in glass melts with a certain composition the influence of the basicity may be neglected [9]. Indeed, the composition of industrial glass melts lies in a very small range of basicity and it seems to be sufficient to discuss the problem without structural considerations. Therefore, the reaction constant of reaction (1) can be written

$$K_{Cr}(T) = \frac{[Cr^{3+}]}{[Cr^{6+}]} p_{O_2}^{3/4} \equiv \exp\left(-\frac{\Delta H_{Cr}^0 - T\Delta S_{Cr}^0}{RT}\right). \quad (2)$$

The interaction between polyvalent elements is considered in different ways in the literature [10 to 14]. The iron-chromium interaction can be easily described as an electron exchange between iron and chromium during cooling according to the reaction

$$3Fe^{2+} + Cr^{6+} \rightleftarrows 3Fe^{3+} + Cr^{3+}. \quad (3)$$

The reaction constant of reaction (3) is given by

$$K(T) = \frac{[Fe^{2+}]^3 [Cr^{6+}]}{[Fe^{3+}]^3 [Cr^{3+}]} \equiv \frac{K_{Fe}(T)^3}{K_{Cr}(T)} \quad (4)$$

where

$$K_{Fe}(T) = \frac{[Fe^{2+}]}{[Fe^{3+}]} p_{O_2}^{1/4} = \exp\left(-\frac{\Delta H_{Fe}^0 - T\Delta S_{Fe}^0}{RT}\right) \quad (5)$$

is the reaction constant of the iron oxidation.

Thus, if the standard reaction enthalpy ΔH^0 and the standard reaction entropy ΔS^0 of the respective oxidation reactions are known, it is possible to calculate the amount of exchanged electrons according to reaction (3). In the case of the iron-chromium interaction the reaction finishes at temperatures sufficiently above the transformation temperature. In this particular case one may consider only the stoichiometric conditions at melt temperatures [12].

3. Experimental

A method of rapid determination of Cr^{6+} has been proposed by Hahn [15]. It is based on acid decomposition in H_2F_2–HCl of about 100 mg samples. After masking excess fluoride ions by boric acid, a blue-violet complex of Cr^{6+} with diphenylcarbazide is formed and its extinction at 540 nm is measured. The decomposition must be carried out in the cold solution, otherwise Cr^{6+} will leave the sample as chromylfluoride. Another method of rapid determination of Fe^{2+} and total iron, also proposed by Hahn [16] is achieved by digestion in H_2F_2/H_2SO_4. After masking of excess fluoride ions the Fe^{2+} ions react in the "status nascendi" to a certain extent with phenanthrolinhydrochloride as a red-colored complex and its extinction at 510 nm is measured. In the same solution the rest of Fe^{3+} will be reduced with ascorbic acid and is determined in the same way. Both methods are easy to practice and have a good reproducibility. The spectroscopic measurements were carried out with a Lambda 19 of Perkin-Elmer, Überlingen (Germany).

For all experiments, a model glass of the composition (in wt%): 70 SiO_2, 20 Na_2O and 10 CaO was melted at 1400 °C for 4 h.

According to the determination of chromium as Cr^{6+} with diphenylcarbazide the detection limit is 2 ppm Cr [17]. By using the rapid method for the Cr^{6+} determination proposed by Hahn in a glass sample melted of crystallized quartz, soda (for analysis) and calcium carbonate (for analysis) in a laboratory melting furnace at 1400 °C for 4 h a blank value of 6 ppm Cr^{6+} (expressed as Cr_2O_3) was obtained. The introduction of these traces of Cr^{6+} from the crystallized quartz can be excluded, because the Cr_2O_3 content in the crystallized quartz is <0.5 ppm. Based on these laboratory glass samples without Fe_2O_3 or Cr_2O_3 additional melts with increasing additions of Fe_2O_3 have been melted. An increasing iron content in the glass significantly increases the Cr^{6+} blank value. It is true that additions of NaH_2PO_4 solution in order to mask the iron ions reduce the blank value, but probably small amounts of the complex formed of iron with diphenylcarbazide can not be prevented (table 1). The analytical results of the redox state of iron in table 1 show that the oxidizing melting conditions are independent of the total iron concentration ($Fe^{2+}/Fe_{tot} \approx 0.1$).

From the laboratory experiments it can be concluded that in presence of 0.25 to 0.5 wt% Fe_2O_3 the blank value for the Cr^{6+} determination according to the proposed analytical procedure lies in the range 10 to 15 ppm in glasses. Comparable iron contents are found in commercial glasses, representing therefore the basis for the discussion of the presented results of the mutual interaction of the ion equilibria Fe^{2+}/Fe^{3+} and Cr^{3+}/Cr^{6+} in glasses.

The reproducibility of the Cr^{6+} determination at 0.2 wt% Cr_2O_3 (as $K_2Cr_2O_7$) was 3 % (20 individual measurements on the same sample). The total chromium content was determined by atomic absorption spectroscopy and atomic emission spectroscopy with induc-

Table 1. Blank values of hexavalent chromium depending on the concentration of Fe_2O_3 (values in brackets refer to samples with iron ions masked by means of NaH_2PO_4)

$[Cr^{6+}]$ given as $[Cr_2O_3]$ in wt%	Fe_2O_3 addition in wt%	Fe_2O_3 concentration in wt%	$[Fe^{2+}]$ given as $[Fe_2O_3]$ in wt%
0.0006 (0.0006)	0	0	0
0.0009 (0.0008)	0.10	0.10	0.01
0.0012 (0.0010)	0.25	0.23	0.02
0.0010 (0.0010)	0.35	0.34	0.05
0.0018 (0.0013)	0.50	0.47	0.05
0.026 (0.0022)	1.00	0.91	0.09

Table 2. Influence of carbon addition on the concentration of hexavalent chromium (0.2 wt% Cr_2O_3 added as $K_2Cr_2O_7$)

carbon addition in wt%	$[Cr^{6+}]$ given as $[Cr_2O_3]$ in wt%	$[Fe^{2+}]$ given as $[Fe_2O_3]$ in wt%	$[Fe_{tot}]$ given as $[Fe_2O_3]$ in wt%
0	0.0700	–	0.006
0.02	0.0480	–	0.23
0.10	0.0380	–	0.23
0.20	0.0080	–	0.23
0.40	(0.0014)	0.011	0.23

Table 3. Varying Fe_2O_3 addition at constant Cr_2O_3 content of 0.2 wt% introduced as $K_2Cr_2O_7$

Fe_2O_3 addition in wt%	$[Cr^{6+}]$ given as $[Cr_2O_3]$ in wt%	$[Cr^{6+}]/[Cr_{tot}]$	$[Fe^{2+}]$ given as $[Fe_2O_3]$ in wt%	$[Fe_2O_3]$ (measured)
0	0.069	0.35	0	0.001
0.25	0.060	0.30	0	0.23
0.50	0.046	0.25	0	0.47
1.00	0.038	0.20	0	0.90

tively coupled plasma, with the results being in good agreement compared with the calculated contents in the batch.

4. Results

4.1 Results of wet chemical analysis

In the concentration range of 0 to 1 wt% of total chromium content the Cr^{6+}/Cr_{tot} ratio will adjust to 0.32 to 0.35, i.e. about 32 to 35% of the total chromium content is present in the hexavalent form. The concentration of Cr^{6+} obtained in glasses from laboratory melts is independent of the type of added chromium, i.e. Cr_2O_3 or $K_2Cr_2O_7$.

In table 2 the influence of increasing portions of graphite on the quotient $[Cr^{6+}/Cr_{tot}]$ for given Fe_2O_3 and Cr_2O_3 contents are shown. The table, however, shows at the same time that at very high amounts of reducing agent (0.4% C) after reduction of hexavalent chromium the bivalent iron is again detectable. The brackets indicate that the Cr^{6+} value equals the blank value which is measured in the presence of iron. Carbon additions in compositions with the chromium carrier Cr_2O_3 prevent the formation of Cr^{6+} in the glass. Reversely, the Cr^{6+}/Cr_{tot} ratio shifts to higher values if 0.5% Na_2SO_4 or $NaNO_3$ is added ($Cr^{6+}/Cr_{tot} = 0.42$).

Independent of the type of chromium added ($K_2Cr_2O_7$ or Cr_2O_3) the Cr^{6+} content decreases at constant total chromium content with increasing iron content for glasses melted under laboratory conditions (table 3). Fe^{2+} is not present in these glasses. On the other hand, in a glass with constant Fe_2O_3 content of 1 wt% the concentration of Fe^{2+} in the glass decreases when the Cr_2O_3 content increases (table 4). It shall be remarked that up to a chromium content (in wt%) of 0.1 at the presence of 1 Fe_2O_3 the typical blank value for hexavalent chromium at 1 Fe_2O_3 is measured (table 1) and the first occurrence of Cr^{6+} in the glass causes a significant change in the measured value for Cr^{6+}.

Based on the results of table 4, in table 5 a Fe^{2+} balance is prepared. Independent of the total chromium concentration a Cr^{6+}/Cr_{tot} value of 0.35 is assumed. In column 6 of table 5 the Fe^{2+}/Fe_{tot} ratio of the sum of the measured Fe^{2+} and the portion oxidized by the

Table 4. Varying Cr_2O_3 addition as $K_2Cr_2O_7$ at constant Fe_2O_3 addition of 1 wt%

$[Cr_2O_3]$ in wt%	$[Cr^{6+}]$ given as $[Cr_2O_3]$ in wt%	$[Cr^{6+}]/[Cr_{tot}]$	$[Fe^{2+}]$ given as $[Fe_2O_3]$ in wt%	$[Fe_2O_3]$ in wt%	$[Fe^{2+}]/[Fe_{tot}]$
0.02	0.0026	–	0.10	0.90	0.11
0.04	0.0024		0.05	0.93	0.05
0.06	0.0025	–	0.03	0.86	0.03
0.08	0.0025	–	0.02	0.91	0.02
0.10	0.0024	–	0	0.95	–
0.15	0.0170	0.11	0	0.93	–
0.20	0.0380	0.20	0	0.97	–

Table 5. Cr^{6+}/Fe^{2+} balance

$[Cr_2O_3]$ addition in wt%	$[Cr^{6+}]$ given as $[Cr_2O_3]$ in wt% (theoretically)	portion Fe^{2+} given as $[Fe_2O_3]$ in wt% oxidized by Cr^{6+} content of column 2	measured $[Fe^{2+}]$ given as $[Fe_2O_3]$ in wt%	$[Fe^{2+}_{tot}]$ of the melt given as $[Fe_2O_3]$ in wt%	$[Fe^{2+}]/[Fe_{tot}]$
0.02	0.007	0.022	0.100	0.122	0.14 (0.90)
0.04	0.014	0.045	0.050	0.095	0.10 (0.93)
0.06	0.021	0.067	0.030	0.097	0.10 (0.96)
0.08	0.028	0.090	0.020	0.110	0.12 (0.91)
0.10	0.035	0.112	0	(0.112)	(0.12 (0.95))
0.15	0.053	0.170	0	(0.121)	(0.13 (0.93))
0.20	0.070	0.224	0	(0.110)	(0.11 (0.97))

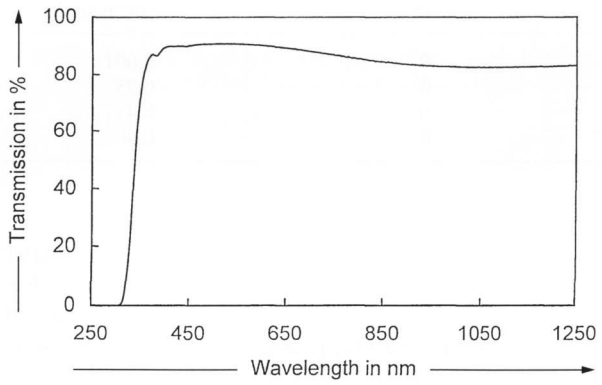

Figure 1. Transmission curve of an iron-containing glass.

hexavalent chromium is given, which is in good agreement with the results of table 1. The table shows that under the selected glass composition and melting conditions a stoichiometric calculation can be applied. Although in the last three glasses no Fe^{2+} is found, a certain portion should have been present in the glass melt. This portion can be calculated from the difference between the expected and the measured Cr^{6+} concentration. These Fe^{2+} concentrations are included in brackets in table 5.

These results obviously show that for chromium-colored green glasses an extremely high amount of Fe_2O_3 (1 wt%) is not sufficient for the compensation of the total oxidation power of Cr^{6+}.

4.2 Photospectrometric results

Figure 1 shows the typical transmission curve for iron-containing but chromium-free glass with the absorption bands at 380 nm (Fe^{3+}) and 1050 nm (Fe^{2+}). The iron-free and chromium-containing glass (figure 2) shows a strong band at 370 nm for Cr^{6+} and at 650 nm for Cr^{3+}. Addition of carbon or Fe_2O_3 (figure 3) leads to the decreasing of the absorption band at 370 nm.

Fe^{2+} is not detectable in these spectra in agreement with the results of chemical analysis. The extremely high extinction coefficient of Cr^{6+} (2550 cm^{-1} wt% $oxide^{-1}$) makes very small amounts of Cr^{6+} visible in a glass (figure 4: Cr^{6+} as Cr_2O_3 = 12 ppm). Also in this curve the Fe^{2+} band is not observed in the presence of Cr^{6+}.

In most cases the results of the spectroscopic investigation and the wet chemical analysis are in good agreement. However, due to the large extinction coefficient of hexavalent chromium the spectroscopic method allows a quantitative determination only at sufficiently low Cr^{6+} concentrations.

4.3 Investigation of commercial green glasses

Within the framework of this publication the Cr^{6+}/Cr^{3+} and Fe^{2+}/Fe^{3+} redox couples in green glass bottles were investigated by the proposed chemical analysis procedure. In table 6 results of the spectroscopic determination and of the wet chemical analysis are shown. In all bottles Fe^{2+} is detectable and the Cr^{6+} value is equal to the blank value of a chromium-free

glass with about 0.5 wt% Fe_2O_3. The transmission curve of a commercial green glass is shown in figure 5, where besides Fe^{2+}, Fe^{3+} and Cr^{3+} bands a determination of Cr^{6+} in agreement with the result of chemical analysis is impossible.

The existence of bivalent iron and the absence of hexavalent chromium lead to the conclusion that technical green glasses have been melted under more reducing conditions than those melted in the laboratory. This refers especially to the content of reducing agent in the natural raw materials, the amount of carbon introduced into the industrial green glass batch as well as the large fraction of cullet. Further laboratory melts have been carried out with Hohenbocka sand, technical soda, Rüdersdorf limestone and technical green glass cullet with 700 ppm C. The Cr^{6+} content (as wt% Cr_2O_3) of glass, on the basis of analytically pure raw materials (0.07 %), is reduced by using the technical raw materials or green glass cullet (50 % in the glass). However, the detectable amount of 27 ppm Cr^{6+} (as Cr_2O_3) is still high compared to the chromium-free glass with 1 wt% Fe_2O_3 (table 1).

From equation

$$4CrO_3 + 3C \Leftrightarrow 2Cr_2O_3 + 3CO_2 \qquad (6)$$

it can be calculated that 100 ppm C in the batch are sufficient to reduce completely the Cr^{6+} ions if 0.2 wt% total Cr_2O_3 are present. An analytical proof of Fe^{2+} in the glasses is regarded as a confirmation of no existence of Cr^{6+} in the glasses.

5. Discussion

In figure 6 the results of tables 3 and 4 are compiled. The presence of hexavalent chromium has been qualitatively checked by means of UV-VIS spectroscopy. Solid symbols mark samples which show hexavalent chromium in the UV-VIS spectrum. The plot shows a decreasing Cr^{6+} content with increasing total iron/total chromium ratio according to reaction (3). After passing a minimum the measured concentration of hexavalent chromium increases again.

The concentration of hexavalent chromium in an iron-free glass melt depends only on the temperature and the oxygen partial pressure. The abscissa intercept in figure 6 can be derived from equation (2):

$$\frac{[Cr^{6+}]}{[Cr]} = \left(\frac{K_{Cr}(T)}{p_{O_2}^{3/4}} + 1\right)^{-1}. \qquad (7)$$

Under the assumption that the reduction of chromium consumes the stoichiometric portion of Fe^{2+}, the intercept of the ordinate is the point where 1 mole of Cr^{6+} is consumed by 3 moles of Fe^{2+}. Combination of equations (2 and 5) then leads to

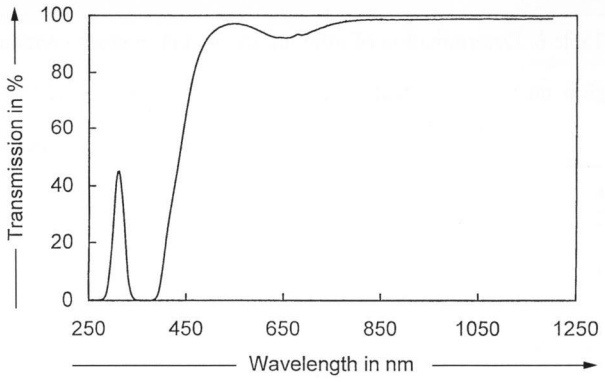

Figure 2. Transmission curve of an oxidizingly melted glass containing chromium.

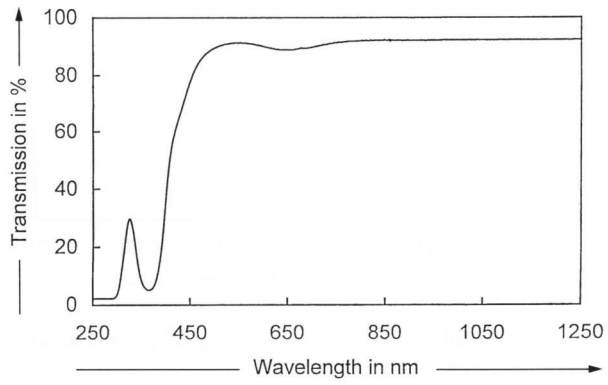

Figure 3. Transmission curve of an oxidizingly melted glass containing iron and chromium.

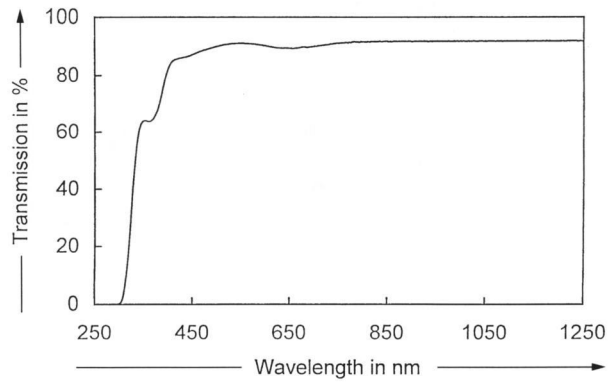

Figure 4. Transmission curve of a glass with a very small amount of hexavalent chromium.

$$\frac{[Fe]}{[Cr]} = 3\left(\frac{p_{O_2}^{1/4}}{K_{Fe}} + 1\right) \cdot \left(\frac{K_{Cr}(T)}{p_{O_2}^{3/4}} + 1\right)^{-1}. \qquad (8)$$

The total iron/total chromium ratio at which all hexavalent chromium is consumed depends also only on the temperature and the oxygen partial pressure. Thus, the theoretical course of the Cr^{6+} decrease is given by a straight line between the abscissa intercept and the ordinate intercept.

Table 6. Determination of iron and chromium in green container glass

glass no.	$[Cr_{tot}]$ given as $[Cr_2O_3]$ in wt%	$[Cr^{6+}]$ given as $[Cr_2O_3]$ in wt% (chemically)	$[Cr^{6+}]$ given as $[Cr_2O_3]$ in wt% (spectroscopically)	$[Fe_{tot}]$ given as $[Fe_2O_3]$ in wt%	$[Fe^{2+}]$ given as $[Fe_2O_3]$ in wt%	$[Fe^{2+}]/[Fe_{tot}]$
1	0.23	0.0013	0	0.37	0.15	0.41
2	0.29	0.0016	0	0.33	0.17	0.52
3	0.29	0.0017	0	0.37	0.15	0.41
4	0.29	0.0016	0	0.37	0.15	0.41
5	0.13	0.0013	0	0.19	0.13	0.68
6 (laboratory)	0	0.0015	0	0.47	0.5	0.11

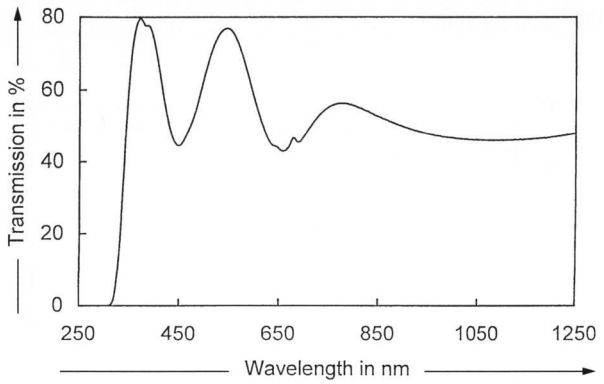

Figure 5. Transmission curve of a commercial green container glass.

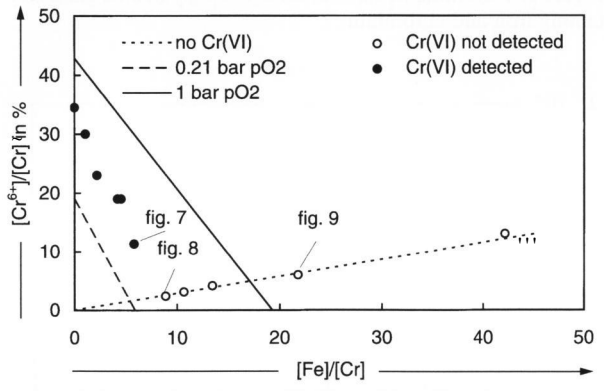

Figure 6. Portion of hexavalent chromium as a function of the iron–chromium ratio.

The oxygen partial pressure has not been measured in the reported investigation and, therefore, must be estimated from the experimental boundary conditions. If the polyvalent elements are introduced in the oxidized state, for instance chromium as $K_2Cr_2O_7$, oxygen excess can be assumed and the melt contains oxygen bubbles. Therefore, the oxygen partial pressure of the sample is 1 bar until all bubbles are expelled. Afterwards equilibration with the surrounding atmosphere by means of diffusion starts. On the other hand, air is included in the batch, thus, the oxygen partial pressure of the glass melt will adjust to that between air and pure oxygen.

In figure 6 the theoretical lines are drawn for 1 and 0.21 bar oxygen partial pressure, respectively. For the calculation of the lines in figure 6 the thermodynamic data for a soda–lime–silica glass [12] have been slightly adjusted in order to achieve the values of $[Fe^{2+}]/[Fe] = 0.1$ and $[Cr^{6+}]/[Cr] = 0.42$, which were measured in the investigated melt under oxidizing conditions for which 1 bar oxygen partial pressure is assumed. Values of $\Delta H^0 = 78$ and $\Delta S^0 = 49$ J/(mol K) for chromium and $\Delta H^0 = 106$ and $\Delta S^0 = 42$ J/(mol K) for iron were used.

As expected from the melting conditions the points in figure 6 are positioned between the lines for 1 and 0.21 bar oxygen partial pressure. With increasing chromium and decreasing iron content the results tend to the direction of higher oxygen partial pressure. At 1 bar oxygen partial pressure nearly 60% of chromium and 10% of iron are in the reduced state. If both are introduced in their oxidized form, $K_2Cr_2O_7$ and Fe_2O_3, potassium dichromate provides considerably more oxygen than hematite. Thus, at high chromium content the results are nearer to 1 bar oxygen partial pressure, while with increasing iron content the results come nearer to the 0.21 bar curve. In summary, the plot in figure 6 is in full agreement with the expected behavior.

Reaction (3) is assumed to finish above the transition temperature, i.e., the consumption of bivalent iron and hexavalent chromium should occur in stoichiometric proportions. This behavior is documented in table 5. Indeed, the Fe^{2+} concentration shows a corresponding behavior as a function of the total chromium/total iron ratio. This means that the existence of Fe^{2+} is synonymous with the absence of Cr^{6+} and vice versa. Thus, the apparent increase of measured hexavalent chromium after passing the minimum is due to the increasing iron concentration, which has been demonstrated in table 1. Figures 7 to 9 show the UV-VIS spectra of some points in figure 6. The sample in the region of Cr^{6+} presence shows a distinct absorption in the UV spectrum. The sample which designs the minimum of the Cr^{6+}/Cr ratio in figure 6 still shows a very small absorption at the position of the Cr^{6+} band, however, it is too small to determine the Cr^{6+} concentration quantitatively, i.e. below 10 ppm. All other samples on the dashed line show no hexavalent chromium in the spectrum, but an absorption

at the Fe^{2+} band. Thus, the dashed line in figure 6 is the blank line of the proposed quantitative Cr^{6+} analysis procedure in iron-containing glasses.

Figure 6 makes it clear that above a certain iron/chromium ratio for thermodynamic reasons no Cr^{6+} can exist in glasses. According to equation (8) this limit depends on the oxygen partial pressure of the melt at a given temperature. This limit can be applied to industrial melting conditions. Figure 10 shows besides the limit of the Cr^{6+} existence as a function of the oxygen partial pressure measured in the feeder channel at 1250 °C and the chromium/iron ratio, the position of some industrial container glass melts. Black symbols mark results for which the absence of Cr^{6+} is checked by means of the proposed analyzing method. All results are found to be in the region where all the Cr^{6+} ions are consumed by Fe^{2+}. However, the use of recycled cullet in flint glass leads to an increased chromium concentration and a further increase can possibly cause some problems under too oxidizing conditions. In that case continuous monitoring of the oxygen partial pressure in the melt helps to avoid Cr^{6+} in the final glass.

6. Summary

Laboratory melts containing different amounts of iron and chromium have been carried out. The melted glasses were investigated with respect to Fe^{2+} and Cr^{6+}. Therefore, wet chemical and spectroscopic methods have been applied. Especially, the used wet chemical analysis enables one to measure hexavalent chromium quantitatively. The Cr^{6+} blank value of the applied method depends significantly on the iron content. An influence of the wet chemical intervention in the structure of the solid glass on the analysis results due to a shift of the ionic equilibrium has not been observed.

Independent of the chromium carrier Cr_2O_3 or $K_2Cr_2O_7$ iron-free glasses exhibited the same Cr^{6+} content of 35 wt% of total chromium. Additions of Na_2SO_4 or $NaNO_3$ increased the Cr^{6+} content up to 42 wt%. Under laboratory conditions the Cr^{6+} concentration decreased with increasing Fe_2O_3 content. Fe^{2+} was not found in the glasses melted from analytically pure raw materials containing less than 0.25 wt% Fe_2O_3 and 0.2 wt% Cr_2O_3, while Cr^{6+} was detectable. Under reducing conditions, i.e. graphite addition, with Cr_2O_3 as chromium carrier, Cr^{6+} was not detectable. By introducing potassium dichromate as chromium carrier and increasing graphite addition, the Cr^{6+} content has been significantly reduced or even completely suspended.

The observed behavior can easily be explained by an electron exchange between iron and chromium during cooling. Due to this reaction chromium oxidizes iron. At a sufficiently high Fe^{2+} concentration in the glass melt Cr^{6+} is totally reduced. The reaction is finished at sufficiently high temperatures, thus, a stoichiometric consideration of the reaction is possible.

In commercial green glasses Fe^{2+} was always detected, while Cr^{6+} was not found. Fe^{2+}/Fe_{tot} ratios of these glasses indicate that they were melted under sufficiently reducing conditions. The same result is found in industrially melted flint and green glasses with known oxygen partial pressure. In the case of the observed iron/chromium ratios the existence of hexavalent chromium can be excluded for all glasses investigated.

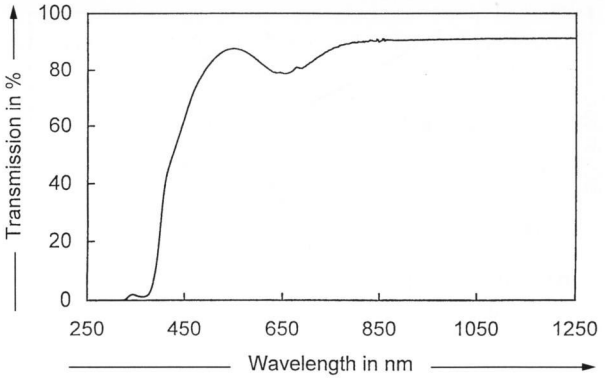

Figure 7. Transmission curve of a glass in the region of Cr^{6+} existence (see figure 6).

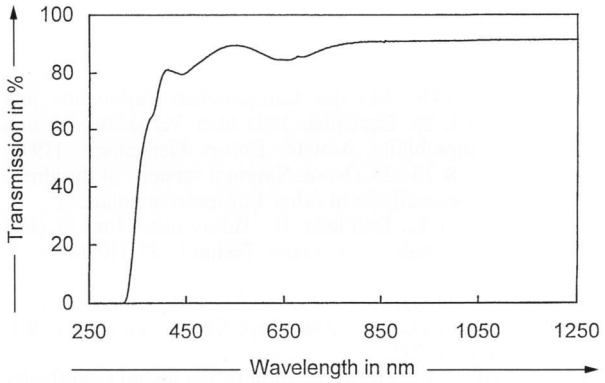

Figure 8. Transmission curve of a glass in the minimum of the ratio $[Cr^{6+}]/[Cr]$ in figure 6.

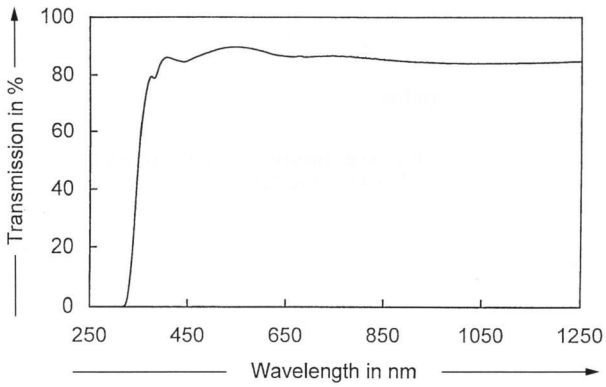

Figure 9. Transmission curve of a glass without Cr^{6+} (see figure 6).

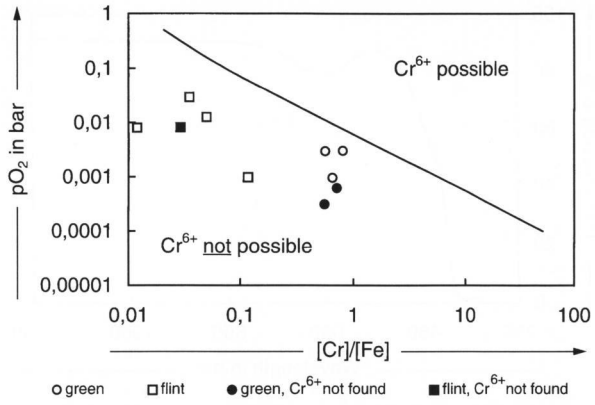

Figure 10. Region of existence of hexavalent chromium depending on oxygen partial pressure and iron–chromium ratio and examples of industrial green and flint container glasses.

7. References

[1] Richtlinie 94/62/EG des Europäischen Parlaments und des Rates v. 20. Dezember 1994 über Verpackungen und Verpackungsabfälle. Amtsbl. Europ. Gemeinsch. (1994) Nr. L 365, S. 10–23. (Note: National versions of this directive are also available in other European languages.)

[2] Guadagnino, E.; Dall'Igna, R.: Heavy metal ions in glass and related legislation. Glass Technol. **37** (1996) no. 3, p. 76–79.

[3] Nath, P.; Douglas, R. W.: Cr^{3+}–Cr^{6+} equilibrium in binary alkali silicate glasses. Phys. Chem. Glasses **6** (1965) no. 6, p. 197–202.

[4] Bamford, C. R.: The application of the ligand field theory to coloured glasses. Phys. Chem. Glasses **3** (1962) no. 6, p. 189–202.

[5] Paul, A.: Optical absorption of chromium (II) in glasses. Phys. Chem. Glasses **15** (1974) no. 4, p. 91–94.

[6] Brückner, R.; Sammet, M.; Stockhorst, H.: Evidence of structural anisotropies in silicate glass fibres by ESR. J. Non-Cryst. Solids **40** (1980) p. 273–289.

[7] Garifyanov, N. S.: Electron paramagnetic resonance of Cr^{6+} in glasses. Sov. Phys. – Solid State **4** (1963) p. 1795–1797.

[8] Paul, A.; Upreti, G. C.: EPR and optical absorption of Cr^{3+} in binary Na_2O–B_2O_3 glasses. J. Mater. Sci. **10** (1975) p. 1149–1153.

[9] Baucke, F. G. K.; Duffy, J. A.: Redox reactions between cations of different polyvalent elements in glass melts: an optical basicity study. Phys. Chem. Glasses **34** (1993) no. 4, p. 158–163.

[10] Kühl, C.; Rudow, H.; Weyl, W.: Oxydations- und Reduktionsgleichgewichte in Farbgläsern. Sprechsaal **71** (1938) no. 7, p. 91–93; no. 8, p. 104–106; no 9, p. 117–118.

[11] Hirashima, H.; Yoshida, T.; Brückner, R.: Redox equilibria and constitution of polyvalent ions in oxide melts and glasses. Glastech. Ber. **61** (1988) no. 10, p. 283–292.

[12] Müller-Simon, H.: Electron exchange reactions between polyvalent elements in soda–lime–silica and sodium borate glasses. Glastech. Ber. Glass Sci. Technol. **69** (1996) no. 12, p. 387–395.

[13] Schreiber, H. D.; Peters, L. J.; Beckman, J. W. et al.: Redox chemistry of iron–manganese and iron–chromium interactions in soda lime silicate glass melts. Glastech. Ber. Glass Sci. Technol. **69** (1996) no. 9, p. 269–277.

[14] Knupp, R. C.; Berger, D. F.: Effects of iron in ultraviolet absorbing green glass. Glass Ind. **47** (1966) no. 5, p. 252–256, 279, 281.

[15] Hahn, B.: Empfindliche und schnelle Methode zur Bestimmung von Cr(VI) in Natron-Kalk-Silikat-Gläsern. Document no. 19b-94 of subcommittee "Glasanalyse" of the Technical Committee I of the German Society of Glass Technology (DGG). Frankfurt/M. 1994.

[16] Hahn, B.: Pers. commun.

[17] Lange, J.: Chemische Analyse glasiger Systeme. Leipzig: Dtsch. Verl. Grundstoffind., 1991. p. 123.

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