Original Paper

Recommended procedure for the IR spectroscopic determination of water in soda-lime-silica glass

Report of the International Commission on Glass (ICG) Technical Committee 14 "Gases in Glass"

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The paper illustrates a procedure recommended by Technical Committee 14 (TC14 "Gases in Glass") of the International Commission on Glass (ICG) for the determination of the water content of soda-lime-silica glass by infrared transmittance spectroscopy, based on the two bands at 2.8 and 3.6 μm using as extinction coefficients 70 and 150 l/(mol · cm), respectively. As shown by the result of two intercomparisons, the agreement on the determined water concentration values can be quite satisfactory, within ±20 ppm, provided the procedure to evaluate the spectral curves is closely specified. The selected extinction coefficients are in reasonable agreement with recent evidence obtained using Nuclear Reaction Analysis.

Empfohlenes Verfahren für die IR-spektroskopische Bestimmung des Wassergehaltes von Kalk-Natronsilicatgläsern

Die Arbeit beschreibt ein vom Technical Committee 14 (TC14 „Gase im Glas") der International Commission on Glass (ICG) empfohlenes Verfahren zur Bestimmung des Wassergehaltes von Kalk-Natronsilicatgläsern durch Infrarot-Transmissionsspektroskopie, das auf der Auswertung der Banden bei 2,8 bzw. 3,6 μm beruht. Als Extinktionskoeffizienten werden die Werte 70 bzw. 150 l/(mol · cm) verwendet. Die Ergebnisse zweier Ringversuche zeigten, daß die Übereinstimmung der ermittelten Wassergehalte mit Abweichungen kleiner als ±20 ppm zufriedenstellend ist, vorausgesetzt, daß das Verfahren zur Spektrenauswertung genau festgelegt ist. Die Ergebnisse stimmen sehr gut mit den Ergebnissen neuester Messungen mit Hilfe der Kernreaktionsanalyse (NRA) überein.

1. Historical background

In the last decade the interest of Technical Committee 14 (TC14 "Gases in Glass") of the international Commission on Glass (ICG) was often focused on water in glass: two round robins for the determination of the water content of various glasses were performed and proposals for a standardized procedure for water analysis based on room-temperature infrared (IR) spectroscopy were considered. On 9 June 1997 in Växjö (Sweden), TC14 organized the "Forum on Water in Glass" during the 4th Conference of the European Society of Glass Science and Technology (ESG) "Fundamentals of Glass Science and Technology". The aim was to highlight the technological relevance of water in glass, to improve exchanges of information and cooperation between experts and to better define some critical areas where the present knowledge was not fully satisfactory. An Organizing Committee including F. Geotti-Bianchini (forum chairman); A. J. Faber; H. Kobayashi and I. Smith (TC14 chairman) finalized the program, outlined the details of the organization and designated the invited speakers. The following presentations were dedicated to the analysis of water in glass:

- F. Geotti-Bianchini (Stazione Sperimentale del Vetro (SSV), Murano-Venice (Italy): A proposal for a TC14 recommended procedure for the IR spectroscopic analyisis of water in soda lime glass [1];
- U. Harder, H. Geißler, M. Gaber, M. Hähnert (Bundesanstalt für Materialforschung und -prüfung, Berlin (Germany)) and O. Dersch, F. Rauch (Univer-

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sity of Frankfurt/M. (Germany)): Determination of the water content of alkali lime silica glasses by IR spectroscopy and vacuum hot extraction method using nuclear reaction analysis for calibration [2];

- F. W. Krämer, R. Haspel, C. Ottermann (Schott Glaswerke, Mainz (Germany)), and S. Ilievski, M. Laube, R. Rauch (University of Frankfurt/M. (Germany)): Measurement of water in industrial glasses by IR spectroscopy and Nuclear Reaction Analysis (NRA) [3].

No proceedings of the meeting were published. In view of the outcome of the discussion, considering both the proposal presented by Geotti-Bianchini [1] and the new evidence presented by Harder et al. [2] and by Krämer et al. [3], TC14 decided to adopt the proposal based on the two-band method. This method is restricted to soda-lime-silica glass and explicitly excludes borosilicate glass and other significantly different chemical compositions such as lead oxide glass. The present paper was produced at the request of TC14 with the purpose to outline the detailed procedure and to present the results of the TC14 round robins along with evidence concerning the extinction coefficients for the spectroscopic procedure.

2. Introduction

A range of articles are produced industrially from soda-lime-silica glass i.e. containers, tableware, float glass, technical glass, fibres and decorative articles. The hydroxyl (OH) content of soda-lime-silica glass melts has a significant influence on their spectral properties, due to the absorption bands near 3 µm, as well as on the low-temperature viscosity. Therefore, significant variations in the hydroxyl content might affect both the melting behaviour (changing the rate of heat transfer from the flame to the melt) and the forming behaviour (altering both the rheology and the radiation heat exchange between the hot article and its environment). In order to confirm this hypothesis, it is necessary to monitor the glass OH content regularly, with the absorption bands in the 2 to 5 µm range providing a suitable tool.

Modern commercial spectrometers need only simple sample preparation (polished plates) and provide a quick, easy and reproducible method to obtain transmittance curves which do not require highly skilled technicians or cumbersome experiments. In spite of these advantages their widespread industrial adoption has so far been hindered by the lack of a harmonized elaboration procedure. This is due to the confusing variety of extinction coefficients and procedures to read the absorption bands from the curves accumulated in the literature.

For internal comparisons even relative water concentration values are acceptable giving differences and variations from the "norm" which can be appreciated. However, problems arise when trying to compare data with external sources. Assessing the influence of OH variations on physical properties is not an easy task, since the effects are small and masked by concurrent random variations in chemical composition and redox. Nonstandardized determinations of concentration values further complicate the task and limit the value of literature data, in view of the difficulty of interrelating them on a common basis.

The present proposal approved by TC14 has the purpose to describe a standard method suitable for industrial use. A detailed procedure will be outlined and its reproducibility and accuracy will be discussed. Hopefully in the future referring to its use will allow a safe intercomparison of data for technological applications.

3. Spectroscopic procedure for water analysis

3.1 Band attribution and nomenclature

The present treatment is based on the band attribution suggested by Scholze [4]. The incorporation of water in silicate glasses takes place according to the reactions:

$$H_2O + SiO{-}Si = 2\,Si{-}OH \qquad (1)$$

$$H_2O + SiO{-}M = M{-}OH + Si{-}OH \qquad (2)$$

where M = network modifier, e.g. Na or $\frac{1}{2}$Ca. According to this mechanism water from the atmosphere and the batch enters the glass structure as silanol groups (Si−OH). Equations (1) and (2) justify the equivalent terms "silanols (or hydroxyls) incorporated in the glass structure" and "water in glass". The first is more correct in view of the chemical bonds formed, the second is justified by the fact that the concentration is expressed in terms of weight percent water, or water released per unit glass volume in the case of a hypothetical complete dehydration (reversing equations (1) and (2)). The presence of molecular water in the bulk is excluded for industrial soda-lime-silica glass, having a water content below 1.0 wt% [5 and 6]. According to their bonding situation, silanol groups give rise to different absorption bands:

- very weakly associated Si−OH units occupying network cavities produce a hydroxyl band with absorption maximum near 2.8 µm (Scholze's "free hydroxyl band" [4]);
- Si−OH units forming hydrogen bonds with neighbouring nonbridging oxygens ($Si{-}O^-$) produce the "first bonded hydroxyl band" with maximum near 3.6 µm;
- a "second bonded hydroxyl band" with maximum near 4.3 µm due to Si−OH in isolated tetrahedra (M_3SiO_3OH) interacting with a neighbouring nonbridging oxygen can be observed only with special spectral elaboration procedures [4 and 5].

The band shape, degree of overlapping and position of the maxima vary with the glass composition [4 and

5]. For simplicity, they will be conventionally designated as 2.8, 3.6 and 4.3 µm bands. Wavelength data are used here only for historical reasons, being inherent in Scholze's treatment [4]. Actually, spectrophotometric measurements yield transmittance curves as a function of wave numbers, $\tilde{\nu}$. The correlation with wavelength, λ is:

wave number in $\text{cm}^{-1} = 10^4$/wavelength in µm.

3.2 Historical development of the spectroscopic procedure

A method to quantify the three hydroxyl bands, assigning to each of them a suitable extinction coefficient, was developed by Scholze on the basis of comprehensive IR spectroscopy and vacuum degassing studies [4]. All the later publications on this subject [7 to 12] nominally adopted Scholze's method. However, each of them introduced a range of adaptations and modifications, so that it is often difficult to read from a given published spectral curve the same OH concentration as that declared by the author. The main sources of discrepancy are:

a) the extinction coefficients (Scholze [4] provided individual values for selected compositions, including some similar to industrial soda-lime-silica glass, and an average value for silicate glasses; later authors adopted selected data, obtained further values on the basis of degassing experiments or suggested new average or rounded values on the basis of literature reviews);

b) the procedure to read the baseline and the OH absorption (Scholze [4] suggested to take into account the mutual band overlapping without disclosing details; later authors with only some exceptions [2 and 11] generally avoided the deconvolution, regarded as cumbersome and subjective, and read the baseline and the maximum absorption directly from the uncorrected spectral transmittance curves);

c) the duplicity of the "two-band" versus "single-band" procedure (Scholze [4] suggested a rigorous method based on the 2.8 and 3.6 µm bands and a simplified method for routine industrial controls based on the 2.8 µm band only, assuming that the ratio of the OH present in the two bands remains constant; most later authors adopted the single-band method).

Further problems arise from the fact that most analytical procedures were developed for laboratory glasses: industrial glasses may differ widely in terms of the composition, the fining practice, the background absorption (due to powerful chromophores such as Fe^{2+}) and the ratio of the 2.8 and 3.6 µm bands. Details of the complex history of the spectroscopic procedure are discussed in [5].

3.3 Description of the proposed harmonized spectroscopic procedure

The spectroscopic procedure approved by TC14 is an adaptation of Scholze's two-band method [4]. The concentration of free and bonded silanol groups is determined separately from the absorption bands at 2.8 and 3.6 µm with suitable extinction coefficients and added together. In view of the difficulty to measure directly the second bonded hydroxyl band at 4.3 µm, its presence is accounted for by increasing by one third the concentration of bonded OH at 3.6 µm. The background absorption and the maximum absorption of the two bands are read directly from the measured spectral curves. A plate with plane and parallel surfaces is obtained from the glass article by grinding and polishing. Its spectral transmittance at normal incidence is measured with a spectrophotometer at 2.5 µm (where the absorption due to OH is considered negligible) and at the transmittance minima (absorption maxima) near 2.8 and 3.6 µm respectively designated $T_{2.5}$, $T_{2.8}$ and $T_{3.6}$. The water concentration $c_{\text{H}_2\text{O}}$ is calculated according to:

$$c_{\text{H}_2\text{O}} = \frac{1}{d}\left(\frac{\lg(T_{2.5}/T_{2.8})}{\varepsilon_{2.8}} + \frac{4}{3}\,\frac{\lg(T_{2.5}/T_{3.6})}{\varepsilon_{3.6}}\right) \qquad (1)$$

where $c_{\text{H}_2\text{O}}$ (in $\text{mol} \cdot \text{l}^{-1}$) is the concentration of water in glass expressed in mol H_2O/l of glass; d the sample thickness in cm; $T_{2.5}$, $T_{2.8}$ and $T_{3.6}$ are measured spectral transmittance values; $\varepsilon_{2.8}$ is the extinction coefficient at the maximum of the 2.8 µm band, 70 l/(mol · cm); $\varepsilon_{3.6}$ the extinction coefficient at the maximum of the 3.6 µm band, 150 l/(mol · cm);

The accuracy of the results depends critically on the following recommendations:

- select a sample thickness allowing maximum band depth without incurring saturation (i.e. with minimum transmittance > 0.1);
- check the stray light, if > 0.01, substract from the spectral transmittance values;
- perform thickness and spectral transmittance measurements on the same area, averaging the result of four measurements of d, $\lg(T_{2.5}/T_{2.8})$ and $\lg(T_{2.5}/T_{3.6})$ in order to average out random errors and to evaluate the reproducibility;
- in order to smooth out errors due to positioning and sample imperfections, reposition the sample for each transmittance measurement, rotating it around its horizontal and vertical axis;
- discard or repolish samples for which four thickness measurements at the corners and one at the centre of the area for transmittance measurements suggest the presence of significant wedge and/or lens errors;
- as far as possible select samples free of surface blemish, bubbles, cords and colour streaks;
- measurements are possible also on curved samples (e.g. sections of tubing or bottle sidewalls), but special precautions are recommended to minimize beam deflection and thickness errors. Samples should be selected free of evident defects, with a thickness as uniform as possible and with the largest available radius of curvature. The edges should be cut or

ground to allow steady positioning and repeated measurements made repositioning the sample each time.

For studies of technological interest it is customary to express the water concentration in terms of parts per million water by weight, c_{ppm}. The conversion is performed according to:

$$c_{\mathrm{H_2O,ppm}} = \frac{c_{\mathrm{H_2O}} \cdot 18000}{\varrho} \tag{2}$$

where 18 000 is a constant taking into account the molecular weight of water and the conversion from litres to grams of glass and from weight fraction to parts per million; and ϱ is the glass density (in g/cm^3).

For most container and float glasses the error introduced by assuming a standard value of density of 2.5 g/cm^3 is negligible (within ±1 %), but for other compositions the actual value should be used.

3.4 Alternative formulations of the procedure

Some operators prefer to perform the spectroscopic measurements in the absorbance mode, determining the spectral absorbance at 2.5 μm, $A_{2.5}$, and at the maxima near 2.8 and 3.6 μm, $A_{2.8}$ and $A_{3.6}$, respectively. Considering that the spectral absorbance is defined as $A_\lambda = \lg(1/T_\lambda)$, then equation (1) is modified as:

$$c_{\mathrm{H_2O}} = \frac{1}{d}\left(\frac{A_{2.8} - A_{2.5})}{\varepsilon_{2.8}} + \frac{4}{3}\,\frac{A_{3.6} - A_{2.5}}{\varepsilon_{3.6}}\right) \tag{3}$$

where $c_{\mathrm{H_2O}}$ (in mol · l^{-1}) is the concentration of water in glass expressed in mol $\mathrm{H_2O}$/l of glass; d the sample thickness in cm; $\varepsilon_{2.8}$ the extinction coefficient at the maximum of the 2.8 μm band, 70 l/(mol · cm); and $\varepsilon_{3.6}$ the extinction coefficient at the maximum of the 3.6 μm band, 150 l/(mol · cm).

In other cases data are available in terms of the spectral absorption coefficient, α_λ, defined by equation (4):

$$\alpha_\lambda = -\frac{1}{d}\ln(T_\lambda/T_0) \tag{4}$$

where d is the sample thickness in cm; T_λ the measured transmittance; and T_0 the transmittance of a sample with $\alpha_\lambda = 0$ (only reflectance losses).

After determining the values of $\alpha_{2.5}$, $\alpha_{2.8}$ and $\alpha_{3.6}$ equation (1) is rearranged as:

$$c_{\mathrm{H_2O}} = \frac{\alpha_{2.8} - \alpha_{2.5}}{2.30259 \cdot \varepsilon_{2.8}} + \frac{4}{3}\,\frac{\alpha_{3.6} - \alpha_{2.5}}{2.30259 \cdot \varepsilon_{3.6}} \tag{5}$$

where $c_{\mathrm{H_2O}}$ (in mol · l^{-1}) is the concentration of water in glass expressed in mol $\mathrm{H_2O}$/l of glass; $\varepsilon_{2.8}$ the extinction coefficient at the maximum of the 2.8 μm band, 70 l/(mol · cm); $\varepsilon_{3.6}$ the extinction coefficient at the maximum of the 3.6 μm band, 150 l/(mol · cm); and 2.30259 the coefficient for the conversion from Neperian to decadic logarithms.

3.5 Simplified (single-band) spectroscopic procedure

The single-band procedure determines the total concentration of silanol groups from the absorption band at 2.8 μm only with a suitable extinction coefficient, the so-called "practical extinction coefficient" [4], assuming that the distribution of free and bonded silanol groups remains constant. After measuring spectrophotometrically the transmittances $T_{2.5}$ and $T_{2.8}$, the water concentration is calculated according to:

$$c_{\mathrm{H_2O,s}} = \frac{1}{d}\left(\frac{\lg(T_{2.5}/T_{2.8}}{\varepsilon_{\mathrm{pract,2.8}}}\right) \tag{6}$$

where $c_{\mathrm{H_2O,s}}$ (in mol · l^{-1}) is the concentration of water in glass expressed in mol $\mathrm{H_2O}$/l of glass; according to the single-band procedure; d the sample thickness in cm; $\varepsilon_{\mathrm{pract,2.8}}$ the "practical" extinction coefficient [4] at the maximum of the 2.8 μm band, i.e. the molar extinction coefficient assumed to represent the absorption of all hydroxyl groups (weakly and strongly associated), 40 l/(mol · cm).

The value of 40 l/(mol · cm) was suggested by the Physical Properties Committee of the UK Society of Glass Technology [9] as an average between the values suggested in [4, 7 and 8] ranging between 37 and 43 l/(mol · cm).

4. Intercomparisons of water analysis

An estimate of the overall errors affecting the determination of the water concentration is obtained by evaluating two interlaboratory comparisons organized by TC14 in 1990 and 1996. Two sets of industrial soda-lime-silica glass samples were distributed. Participants were requested to prepare polished plates and to determine the water content spectrophotometrically, without the procedure being specified.

The evaluation of the interlaboratory agreement is based on the results obtained with the single-band method, which were reported by the majority of participants, corrected on the basis of a common extinction coefficient of 40 l/(mol · cm). In Table 1 are reported for each sample the average water content and the absolute standard deviation, which ranges between ±7 and ±15 ppm. With the participants free to select the extinction coefficient the spread was up to ±40 ppm. This result exemplifies dramatically the advantage of adopting a common elaboration procedure.

Table 1. Results of TC14 interlaboratory comparisons, expressed as average water concentration values c_{H_2O} with root mean square deviations σ (both in ppm), corrected on the basis of an extinction coefficient = 40 l/(mol · cm)

intercomparison	first (1990)		second (1996)	
number of participants	6		6	
sample	float glass	cast glass	container glass	container glass
description	gas-fired, clear	gas-fired, amber	gas-fired, amber	oxycombustion, amber
c_{H_2O}	345	302	353	527
σ	±12	±15	±9	±7

In 1982 similar results were obtained in the course of an intercomparison set up by the Physical Properties Committee of the UK Society of Glass Technology [5 and 9]. Three samples of float and container glass were circulated between eight laboratories. On the basis of a common elaboration procedure and extinction coefficient (40 l/(mol · cm)) the spread was within ±18 ppm.

5. New evidence about the extinction coefficient of soda-lime-silica glass

The determination of the extinction coefficient of a glass with a given composition requires preparing samples with different OH levels and determining accurately their spectral transmittance curves and the water concentration using independent methods. In principle the water content can be determined by vacuum degassing or thermal outgassing with an inert carrier gas followed by chemical, gravimetric or mass spectrometric quantitative analysis of the released water [4, 7, 8, 11 and 13]. The procedure is generally cumbersome and extremely sensitive to a range of artefacts due to the contemporary release of other gases (and oxides) and to the risk that the released water may condense again in the apparatus before reaching the detector or trap. In spite of these difficulties the available values for soda-lime-silica glass are in reasonable agreement: 41 and 39 l/(mol · cm) for a glass with composition (in wt%) $74SiO_2$, $16Na_2O$, 10CaO [4 and 7]; 43 and 37 l/(mol · cm) for two glasses with composition (in wt%) $72SiO_2$, $13.5Na_2O$, 12.7CaO, $1.5Al_2O_3$, and $74SiO_2$, $16Na_2O$, 5CaO, 3.5MgO, $1.4Al_2O_3$, respectively [8].

A direct determination of water in glass was attempted in the sixties using Nuclear Magnetic Resonance (NMR) to detect the hydrogen nuclei; however, the scatter of results [7 and 14] discouraged further attempts for a long time. Recently a new campaign was launched using Nuclear Reaction Analysis (NRA) [15 to 19]. In the course of the Forum on Water in Glass the presentations of Harder et al. [2] and Krämer et al. [3] illustrated new evidence obtained at the University of Frankfurt/Main by Prof. Rauch's group. The sample is irradiated by a ^{15}N ion beam whose penetration depth varies with the beam energy. A nuclear reaction takes place between the hydrogen atoms and the ^{15}N ions: $^{1}H(^{15}N, \alpha\ \gamma)^{12}C$. As a result of this reaction γ rays of a certain energy are emitted. The yield of characteristic γ rays is measured as a function of the beam energy of the ^{15}N ion beam. In this way it is possible to obtain a hydrogen depth profile. Near the surface the hydrogen concentration is higher due to glass hydration caused by atmospheric humidity, at greater depths it declines until it reaches a plateau (at a depth of 50 to 100 nm). The bulk water concentration is determined from the hydrogen concentration observed at the plateau. The overall error affecting the hydrogen content is about ±9 %.

Harder et al. [2] prepared three series of alkali-lime-silica glasses with composition (in mol%) $74SiO_2 \cdot 16R_2O \cdot 10CaO$ (R = Na, K, Cs) and a wide range of hydroxyl levels. The IR transmittance was measured and the water concentration was determined with NRA. The water concentration was calculated from the IR spectra with the two-band method according to equation (1) using as extinction coefficients 70 and 150 l/(mol · cm). No band separation procedure was applied. The water concentration calculated in this way was larger by 9 % than that determined with NRA. Using as modified extinction coefficients 76 and 164 l/(mol · cm), respectively, the calculated water concentrations were identical to those determined with NRA. This result shows that NRA is well suited for the calibration of the IR spectrophotometric method.

The practical extinction coefficient at 2.8 μm for the single-band method, calculated by introducing the measured transmittance and the water concentration determined with NRA in equation (6), was 39.8 l/(mol · cm) for soda-lime-silica glass (see also [17]). Krämer et al. analysed some industrial soda-lime-silica glasses by IR spectroscopy and by NRA. Samples included sheet glass, float glass and container glass. For each sample the extinction coefficient at 2.8 μm for the single-band method was calculated by introducing in equation (6) the measured transmittances and the water concentration determined with NRA. The extinction coefficient ranged between 40 and 42 l/(mol · cm) for container glass and between 46 and 51 l/(mol · cm) for float glass. In summary, the results of recent NRA measurements are in

Table 2. Basicity numbers of some industrial and laboratory glasses

type of glass	basicity number
soda-lime-silica	
container glass	33 to 36
float glass	34 to 36
household and technical glass[1]	33 to 37
Muranese hand-worked glass	34 to 36
model glass $74SiO_2 \cdot 16R_2O \cdot 10CaO$	24.2
SiAlNaCa [8]	34.6
SiAlNaCaMg [8]	33.8
others	
borosilicate glass	15 to 20
pure SiO_2	13

[1] Technical glass includes car headlamps, light fixtures, glass blocks, insulators.

reasonable agreement with previous evidence obtained by degassing and with the spectrophotometric method recommended by TC14.

6 Discussion

6.1 Selection of the extinction coefficients

Considering the available published evidence [4, 7 and 8] and the recent NRA studies reported in [2 and 3], TC14 adopted the two-band method selecting for all the soda-lime-glasses the extinction coefficients inserted in equation (1) i.e. 70 and 150 l/(mol · cm).

According to Scholze [4], the extinction coefficient is significantly influenced by the glass composition, in particular by the ratio of network modifiers to formers. A way to estimate the fraction of modifiers is the basicity number, taking into account the mole fraction of each oxide corrected by an acidity coefficient. Details are discussed in [5]. Reported in table 2 are the basicity numbers of some types of industrial soda-lime-silica glass, as well as of the model glass $74SiO_2 \cdot 16R_2O \cdot 10CaO$. The variation range is relatively narrow, at least when compared to pure silica glass and borosilicate glass, with definitely smaller basicity numbers and larger extinction coefficients [8]. In view of these considerations it seems unlikely that the spread observed in [3] in the practical extinction coefficients of float glass obtained from different plants and the differences compared to container glass and the model soda-lime-silica glass studied in [2] may be attributed only to a different chemical composition of the samples. The discrepancies in the practical extinction coefficients can probably be attributed to different calibration procedures (in particular as concerns the elaboration of spectral curves) and different $E_{2.8}/E_{3.6}$ ratios (see section 6.3).

Even in the presence of some discrepancies on the practical extinction coefficients, TC14 adopted a standard conventional value for all the soda-lime-silica glasses. The main application of water concentration data is to predict variations of glass or melt properties (e.g. viscosity) associated with given changes of the OH level. It is immaterial whether the difference in water concentration causing a viscosity decrease corresponding to a decrease of the isochomal temperature of 3 K for a given glass is estimated on the basis of a "realistic" or "conventional" extinction coefficient, or even on the basis of $\lg(T_{2.5}/T_{2.8})/d$, as long as the elaboration of the IR spectral curves is well defined and universally adopted. In the future a revision of the standard procedure cannot be excluded, provided new, consistent and scientifically recognized data about the extinction coefficients is available.

6.2 Accuracy of the recommended procedure

For the calculation of the water concentration equation (1) requires measurement of the thickness d, $\lg(T_{2.5}/T_{2.8})$ and $\lg(T_{2.5}/T_{3.6})$. The optimum thickness for accurate transmittance readings (minimizing the uncertainty on $\lg(T_{2.5}/T_{2.8})$ and $\lg(T_{2.5}/T_{3.6})$ associated with an uncertainty of ±0.01 on both $T_{2.5}$, $T_{2.8}$ and $T_{3.6}$) is generally 2 to 3 mm for samples with 300 ppm water. For an ideally plane and parallel plate random errors in thickness readings range from ±0.1 to ±0.01 mm according to the quality of the gauge used, causing a relative uncertainty on c_{H_2O} between ±0.3 and ±5%. Wedge or lens shaped deviations from planarity due to inaccurate grinding increase the uncertainty of thickness measurement. Random spectral transmittance errors are due to sample quality, positioning and reading. Nonplanar surfaces cause beam deflection and defocusing; bubbles and cords deflect and scatter the transmitted beam; poor surface polish and dirt accumulation cause scattering losses. Inaccurate sample positioning causes tilt errors. Further T_λ errors (random and systematic) are due to instrument quality and operation: noise, wavelength and photometric accuracy, interreflections with the detector, stray light, chart or electronic reading and atmospheric absorption [20 to 22]. An empirical estimate of the overall uncertainty on spectral transmittance measurements was attempted by TC14 by organizing an intercomparison of spectral transmittance measurements on a set of three glass plates that were circulated between the participants. Measurements are still being carried out. Preliminary results suggest that the relative discrepancies for T_λ range to to a worrying ±10%, while for $\lg(T_{2.5}/T_{2.8})$ and $\lg(T_{2.5}/T_{3.6})$ they are within ±1%. This much smaller uncertainty is due to the favourable circumstance that most of the above errors due to sample quality, positioning and reading affect in a similar way the spectral transmittance at 2.5, 2.8 and 3.6 µm.

To correct from mol/l to ppm the water concentration must be divided by the glass density according to equation (5). Uncertainties on density have a negligible influence on the concentration if its value is measured or calculated from the chemical composition, but if a nominal value of 2.500 g/cm^3 is used, the error can become significant particularly for compositions including barium, zinc and potassium.

An empirical estimate of the overall uncertainty affecting the water concentration is obtained by evaluating the intercomparisons on water analysis reported above. If the measuring procedure is carefully specified and random errors limited by averaging repeated measurements, discrepancies within ±20 ppm can be achieved. All such uncertainties are small as compared to the systematic differences (up to over ±50 %) arising if:

- the procedure to elaborate the spectral curves is changed;
- the criteria to estimate the background absorption are modified;
- band deconvolution is introduced;
- different extinction coefficients are selected.

For this reason TC14 adopted the rigorously specified procedure outlined in section 3.3 aiming primarily at consistency.

6.3 Two-band versus single-band procedure

As discussed in detail in [5], the agreement between the results of the two-band and single-band procedure, c_{H_2O} and $c_{H_2O,s}$, varies as a function of the distribution of weakly and strongly associated hydroxyls, expressed by the ratio:

$$E_{2.8}/E_{3.6} = \frac{\lg(T_{2.5}/T_{2.8})}{\lg(T_{2.5}/T_{3.6})} \ . \qquad (7)$$

The concentrations c_{H_2O} and $c_{H_2O,s}$ calculated according to equations (1) and (6) are identical only for the glass for which the simplified procedure was developed, with $E_{2.8}/E_{3.6} \approx 0.83$. For other situations the relative difference between the results of the two procedures is:

$$\frac{c_{H_2O} - c_{H_2O,s}}{c_{H_2O}} = \frac{-1.2054 \cdot E_{2.8}/E_{3.6} + 1}{1.6071 \cdot E_{2.8}/E_{3.6} + 1} \ . \qquad (8)$$

For industrial soda-lime-silica glasses the ratio $E_{2.8}/E_{3.6}$ varies according to table 3. According to table 3 and equation (8) for containers and float glass the agreement between the two procedures is within 9 % or 26 ppm, but for other types of glass the difference can range up to 40 %, i.e. it becomes unacceptable. For this reason TC14 adopted as a reference procedure the two-band method. The single-band method is suitable for routine tasks and to compare data with other laboratories adopting it, taking advantage of the possibility to interconvert results with the help of an equation obtained by rearranging equation (8):

Table 3. Ratio $E_{2.8}/E_{3.6}$ for some industrial soda-lime-silica glasses [5] and corresponding difference between the two-band and single-band procedure for c_{H_2O} = 300 ppm

type of glass	ratio $E_{2.8}/E_{3.6}$	$\lvert c_{H_2O} - c_{H_2O,s}\rvert$ in ppm
containers	0.82 to 1.02	2 to 26
float glass	0.84 to 0.99	2 to 22
household and technical glass[2)]	0.57 to 0.75	13 to 49
Muranese hand-worked glass	0.32 to 0.60	42 to 122

[2)] Technical glass includes car headlamps, light fixtures, glass blocks, insulators.

$$c_{H_2O,s} = c_{H_2O}\,\frac{2.8125 \cdot E_{2.8}/E_{3.6}}{1.6071 \cdot E_{2.8}/E_{3.6} + 1} \ . \qquad (9)$$

On the basis of equation (9) quoting the "single-band" concentration, $c_{H_2O,s}$, and the ratio $E_{2.8}/E_{3.6}$ is equivalent to quoting the "two-band" concentration c_{H_2O}.

An attempt to elucidate the factors influencing the ratio $E_{2.8}/E_{3.6}$ is reported in [5]. Both the chemical composition, the redox state of polyvalent ions and the use of fining agents were considered for a wide range of industrial soda-lime-silica glass samples. Probably the ratio $E_{2.8}/E_{3.6}$ is the result of a complex combination of all such factors. Recently some authors suggested that $E_{2.8}/E_{3.6}$ may act as a structural probe, responding to the fraction of modifiers [23]. This is valid in principle when glasses with widely different compositions are compared, or within a homologous glass series melted with a consistent procedure. But within the relatively narrow composition range of industrial soda-lime-silica glass no correlation was found [5] between $E_{2.8}/E_{3.6}$ and the basicity numbers (correlation coefficient 0.1).

6.4 Delimitation of the field of application

The TC14 standardization procedure applies to any soda-lime-silica glass. Excluded are glasses with definitely different formulations such as pure silica glass, lead oxide glass, borosilicate glass and glass for TV screens, for which Williams et al. [8] suggested widely different extinction coefficients, and measurement performed with NRA by Krämer et al. [3] did not provide a consistent extinction coefficient. For compositions with a soda-lime-silica glass base but including substantial amounts of heavier oxides such as K_2O, BaO, ZnO and PbO the standardized procedure can be applied with caution, in the absence of specifically developed extinction coefficients.

For compositions containing substantial amounts of ferrous iron, the spectral transmittance in the range between 2.5 and 3.6 µm progressively decreases, due to the tail of the broadband near infrared absorption of ferrous iron [24]. For example, for a 2 mm plate with FeO above 0.5 wt% the spectral transmittance at 2.5 μm falls below 0.3 (and consequently the transmittance at the OH band maximum falls below 0.15). Therefore, as the FeO content increases, it becomes increasingly difficult to meet the requirement to select a sample thickness allowing maximum OH band depth without incurring saturation. By comparing measurements obtained with NRA and IR it was shown that the influence of the broad NIR band of ferrous iron on the OH bands can be neglected for FeO contents up to 0.5 wt% [25], a condition satisfied by most industrial soda-lime-silica glasses.

In no case should the two-band method be applied to borosilicate glass. A range of spectrophotometric measurements on neutral and technical glass described by [1] showed that the water concentration should be estimated on the basis of the 2.8 μm band only, in agreement with [4]. The curves obtained by subtracting the spectra of two samples with a given composition but different OH levels show only the presence of such band. Comparing the spectral curves of a given borosilicate glass composition, regardless of the water content, the difference $\alpha_{3.6} - \alpha_{2.5}$ is nearly constant. These two results suggest that the other band with maximum at 3.6 μm is due to absorption of the B−O bond.

7. Conclusions

The most important requirement of procedures for the determination of the water content of glass is the possibility to intercompare results with other laboratories. A suitable method is IR spectrophotometry, provided the procedure to evaluate the spectral curves is closely specified.

Two intercomparisons of water analysis showed that using a standardized procedure the water content of soda-lime-silica glass can be determined from the IR transmittance curves with an agreement within ±20 ppm, quite satisfactory for evaluating the influence of water content differences on physical properties and workability.

A spectrophotometric procedure approved by TC14 evaluating the water concentration using suitable extinction coefficients which are in good agreement with recent independent NRA determinations of the water concentration was described. TC14 recommends for the future the consistent adoption of the outlined procedure.

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