

Measuring the low OH content in quartz glass

Bert Sloots

Philips Lighting Quartz and Special Glass Factory, P.O. Box 150, 9670 AD Winschoten, The Netherlands

Received 17 July 2007; received in revised form 8 January 2008; accepted 12 January 2008

Available online 1 February 2008

Abstract

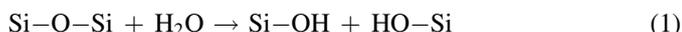
In 1975 Philips Lighting started with the production of quartz glass tubes for lighting applications. The OH content is an important parameter of quartz glass. Every batch quartz glass tubes supplied to a customer is analysed and has a guaranteed OH content. Because there are different methods to measure and calculate the OH content, the ‘Philips Lighting method’ is presented in this paper. Hopefully, this paper sets a standard for the future (low) OH analyses in quartz glass.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Quartz; Hydroxyl; Silanol; OH

1. Introduction

Quartz glass – or so-called vitreous silica – produced by Philips Lighting is highly pure amorphous silicon dioxide. Highly pure quartz sand is melted at >2000 °C in an electric furnace. During melting of quartz sand to quartz glass, OH-groups (“hydroxyl groups”) are built in the quartz network (~ 150 ppm) according to:



OH-groups diffuse out of the quartz glass at elevated temperatures. This phenomenon takes place during burning of the lamp. OH influences the halogen cycle in the lamp and reacts with the metal filament. The lamp lifetime is reduced significantly as result of this phenomenon. In order to reduce the OH content in quartz glass, the material is heated to ~ 1000 °C in a vacuum furnace to extract OH-groups at a predefined concentration.

The Silanol hydroxyl groups are characterised with absorptions at $3800\text{--}3200$ cm^{-1} . There are several types of Silanol: i.e. “free Silanol” and “physical bonded Silanol”. The latter form disappears at temperatures above 200 °C. When quartz glass is heated at approximately 1000 °C, only the “chemical bonded Silanol” remains, with a stretching vibration at ~ 3670 cm^{-1} .

During the first years of manufacturing, Philips measured the OH content with dispersive spectrometers (Jasco IRA-2 and the Philips SP3). All the measurements were calculated by hand, drawing a baseline and measuring the peak height with a ruler. Dispersive spectrometers are double beam, no interference of atmospheric water. In time the sampling frequency increased grew and the OH content was at such a low level that dispersive analysis did not offer enough accuracy. FT-IR was introduced to solve this problem. The Philips PU9800 FT-IR was introduced in 1988. From 1998 onwards the Biorad FTS 175 was used. FT-IR is single beam. With single beam, also after measuring the background, atmospheric water is also measured and low OH absorption cannot be seen nor measured (Fig. 1).

In order to make FT-IR sufficiently accurate, the following procedure was introduced:

- Purge with 40-L/min dry nitrogen gas for about 30 min.
- In order to shorten the measuring time, a 15 position (1 background, 14 samples) sample changer is build, to measure 14 samples in one cycle.

Table 1 shows an overview of the spectrometers, the number of samples, and the OH level that can be detected.

In 2007 a Bruker Vertex 80v FT-IR is used by Philips, with a special configuration to measure the OH content. This configuration consists of:

- vacuum (<1 hPa),
- MIR ceramic source,

E-mail address: bert.sloots@philips.com.

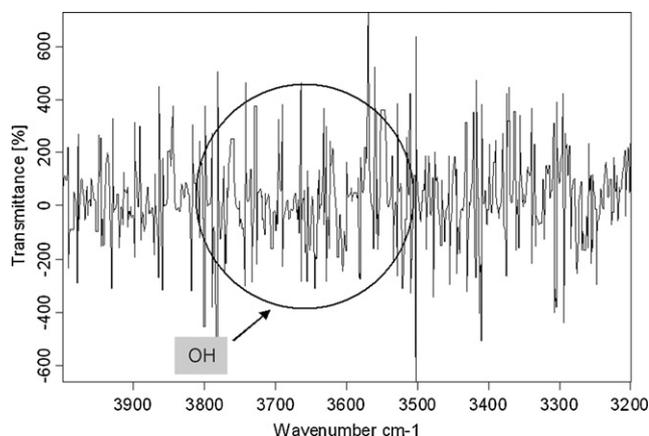


Fig. 1. Measuring in air, also after measuring the background, atmospheric water is also measured and low OH absorption cannot be seen nor measured.

- CaF₂ beam splitter (better than KBr),
- InSb detector (liquid N₂ cooled, with special cold filter, resulting in an increased accuracy compared to the standard InSb detector),
- 15 position sample changer,
- resolution: 4 cm⁻¹,
- special script.

2. Experimental

From quartz tubes (diameter 2–40 mm, wall thickness 0.5–3.0 mm), samples were cut (~25 mm × 10 mm) for analysis. The samples were fixed (with beeswax) on a sample holder or sample wheel with a slit of 2 mm. Tubes with a diameter less than 5 mm, were only cut in longitudinal direction.

The measurement was carried out after placing the sample in the spectrometer. Fig. 2 shows a typical water-free spectrum of a quartz glass sample.

The calculation of the OH content is performed with a “script”. The script has three important features:

- (1) baseline calculation,
- (2) Peak Search,
- (3) calculation of the OH content.

A typical example is explained in the following sections in order to clarify these calculations.

2.1. Baseline calculation

To calculate the OH content an accurate baseline is needed to calculate “peak height” of the OH absorption at

~3670 cm⁻¹. The most accurate baseline is a Spline (Bézier) polynomial [1].

2.2. Peak Search

The following step is Peak Search. With Peak Search the script search determines the largest difference between baseline and spectrum. This value (the so-called “Peak Min”, the minimal transmission or T_{\min}), is needed for calculation of the OH content.

Fig. 2 shows the Spline baseline and the T_{\min} (in this example 94.50%) at ~3670 cm⁻¹.

After this calculation the baseline is normalized at 100% and the peak height is calculated. Fig. 3 shows an example.

2.3. Calculation of the OH content

Based on the results so far, the maximum transmission (T_{\max}) can be calculated according to:

$$T_{\max} = T_{\min} + \text{peak height} \quad (2)$$

The T_{\min} , T_{\max} (in this example: 94.67%) and the sample thickness d (in this example: 1.90 mm) are needed for further calculation.

The next step is to calculate the optical density (β). The optical density is the absorbance from an optical element (glass) by a specific wavelength according the law of Lambert Beer.

$$\beta = \frac{1}{d} \log \left(\frac{T_{\max}}{T_{\min}} \right) \quad (3)$$

With: β in mm⁻¹; d : in mm.

Using the values from the example the optical density (β) is:

$$\beta = \frac{1}{1.90} \log \left(\frac{94.67}{94.50} \right) = 0.00041 \text{ mm}^{-1} \quad (4)$$

The calculation of the OH content is based on a “conversion factor”:

$$\text{OH}(\text{ppm}) = \beta \times \text{factor} \quad (5)$$

$$\text{factor} = \frac{M_{\text{OH}} \times 10,000}{e_{\text{OH}} \times p_{\text{glass}}} \quad (6)$$

With: M_{OH} = molar weight OH⁻ (17 g/mol); p_{glass} = density glass (=2.21 g cm⁻³); e_{OH} the absorption coefficient (in L mol⁻¹ cm⁻¹).

The absorption coefficient can also be interpreted as the absorption of OH at a specific wavelength. The choice of the

Table 1

Overview of the spectrometers, the number of samples, and the OH level that can be detected in the period 1975–2007

Spectrometer	Year	Type	Samples per year	OH level (ppm)	Measuring time (min)
Jasco IRA-2	1975–1981	Dispersive	200	5	20
Philips SP-3	1981–1988	Dispersive	500	2	20
Philips PU9800	1988–1998	FT-IR	3.000	1	10
Biorad FTS 175	1998–2007	FT-IR	14.000	0.2	3
Bruker Vertex 80v	2007	FT-IR	8.000	<0.05	1

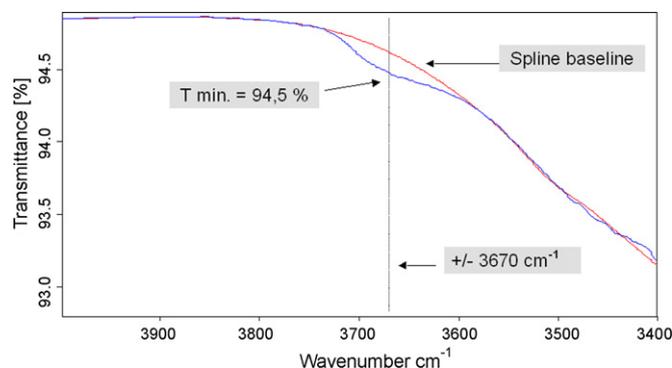


Fig. 2. OH absorption at $\sim 3670\text{ cm}^{-1}$ in atmospheric water-free spectrum after purging or vacuum with Spline baseline.

absorption coefficient is arbitrary, Philips Lighting use the ‘Stephenson’ value [2].

$$993 = \frac{17 \times 10,000}{77.5 \times 2.21} \quad (7)$$

The OH calculation for this specific example is completed by:

$$\text{OH}(\text{ppm}) = 0.00041 \times 993 = 0.41 \quad (8)$$

3. Results

The method for determining the (low) OH content in quartz glass described in the previous sections, has the following characteristics:

- measuring time (14 samples): 15 min,
- accuracy: 0.05 ppm.

The validation (ISO 17025) of a 0.25 ppm OH standard gives the following results:

- limit of detection: 0.03 ppm,
- repeatability: 0.01 ppm,
- reproducibility: 0.01 ppm,
- uncertainty ($k = 2$): 0.02 ppm.

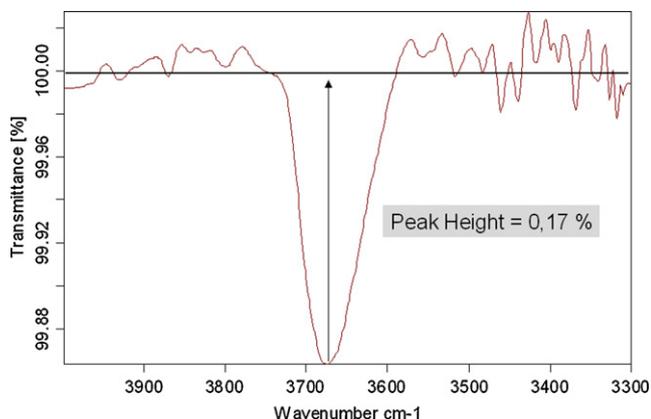


Fig. 3. The baseline is normalized at 100% and the peak height is calculated.

4. Discussion

An OH content measurement with FT-IR is very fast and requires little sample preparation. Also there is a wide range of FT-IR spectrometers available for this kind of analysis. Each FT-IR spectrometer is capable to detect the OH content in quartz glass. With a low-end FT-IR it is possible to measure high-level OH contents (>5 ppm) on a considered manner. A low OH content (<2 ppm) can only be measured with a high-end FT-IR, including an InSb detector and the availability of vacuum or purging with dry N_2 gas.

Despite the fact that high-end spectrometer very capable determining an accurate spectrum in the low OH concentration region, quartz manufacturers use different methods for measuring the OH content.

There are four critical parameters in the calculation procedure, i.e.:

- (1) baseline,
- (2) T_{\min} ,
- (3) T_{\max} ,
- (4) absorption coefficient.

4.1. Baseline

The best baseline for low OH is a Spline baseline.

Using a linear baseline instead of a Spline baseline, the difference is approximately half of the peak height.

4.2. T_{\min}

Because the OH absorption peak shifts slightly depending on the OH concentration, the optimal method is to search for the exact T_{\min} (2.2 Peak Search), instead measuring the T_{\min} at a fixed wavelength.

4.3. T_{\max}

Formula (2) shows the calculation of the T_{\max} . This method enables the measuring of the net OH-peak. Some laboratories measure the T_{\max} in the range of $4000\text{--}3700\text{ cm}^{-1}$. Measuring the T_{\max} in this region results in incorrect OH values, because a part of the silica absorption will be calculated as OH. Quartz with a high OH content ($\sim 25\text{--}50$ ppm) is less susceptible for this error.

4.4. Absorption coefficient

The absorption coefficient for OH in quartz glass is arbitrary. For the OH-peak at 3670 cm^{-1} a wide range of absorption coefficients is reported in literature: $35\text{ L mol}^{-1}\text{ cm}^{-1}$ [3], $58\text{ L mol}^{-1}\text{ cm}^{-1}$ [4], $77.5\text{ L mol}^{-1}\text{ cm}^{-1}$ [2], $100\text{ L mol}^{-1}\text{ cm}^{-1}$ [5], $178\text{ L mol}^{-1}\text{ cm}^{-1}$ [6], $191\text{ L mol}^{-1}\text{ cm}^{-1}$ [7].

The spread in the reported values demonstrates the difficulties encountered in the determination of these values, even in a relatively simple sample such as that of vitreous silica. Some researchers report absorption coefficients in terms of

water; others reported their values in terms of hydroxyl or molecular water. Unfortunately, most papers do not always clearly state which form of water is indicated by the coefficient, so that same ambiguity is often present in the interpreting these values [8]. The experiments of Stephenson and Jack (value: $77.5 \text{ L mol}^{-1} \text{ cm}^{-1}$) are well documented [2]. Stephenson and Jack determined $e\text{OH}$ by studying the weight lost by a Spectrosil sample during firing in vacuum at 1000°C . The loss in weight was related to the optical density. Two experiments gave respectively 78 and $77 \text{ L mol}^{-1} \text{ cm}^{-1}$.

From the beginning of the production of quartz glass, Philips uses the Stephenson value. Van der Steen [4], former head of Process Development Lighting Components of Philips Lighting, reports in his doctoral thesis an $e\text{OH} = 58 \text{ L mol}^{-1} \text{ cm}^{-1}$, by studying the weight lost by a rinsed, milled and melted Brazilian rock quartz sample, during firing in vacuum at 1000°C and concludes that the value he found is not too far from the absorption coefficient determined by Stephenson.

5. Conclusions

Thirty years of OH analysis in quartz glass resulted in thorough and accurate knowledge concerning this subject. In this paper, Philips Lighting presents a method that is reliable and accurate especially for low OH concentrations ($< 2 \text{ ppm}$).

In order to determine OH concentrations in a comparable way, standardization of the method is essential. The method described in this paper is proposed as a standard for measuring low OH concentrations in quartz glass.

We propose the standard method for measuring low OH concentrations in quartz glass:

- high-end FT-IR spectrometer,
- purge 30 min with dry N_2 ($\sim 40 \text{ L/min}$), or use vacuum,
- MIR source,
- CaF_2 beam splitter,
- InSb detector,
- Resolution 4 cm^{-1} ,
- Baseline: spline,
- Search the T_{min} , instead of fixed wavelength,
- Measure/search T_{max} at the same wavelength as T_{min} ,
- Absorption coefficient: $77.5 \text{ L mol}^{-1} \text{ cm}^{-1}$.

Acknowledgement

Thanks to Dr. Martin Pirzer from Bruker—Ettlingen, Germany, for writing the script.

References

- [1] Numerical Recipes in C, William H. Press et al., Cambridge University Press (1988), sbn: 052135465x.
- [2] G.W. Stephenson, K.H. Jack, *Trans. Br. Ceram. Soc.* 59 (1960) 397.
- [3] Borello, et al. *J. Phys. Chem.* 71 (1967) 2938.
- [4] G.H.A.M. Van der Steen, Introduction and Removal of hydroxyl groups in vitreous silica, Philips, Doctoral Thesis (1976).
- [5] R.S. McDonald, *J. Phys. Chem* 62 (1958) 1168.
- [6] G.A. Galkin, et al. *Russ. J. Phys. Chem.* 43 (1969) 1117.
- [7] J. Mathias, et al. *J. Coll. Interf. Sci.* 126 (1988) 61.
- [8] J.E. Shelby, *Handbook of Gas Diffusion in Solids and Melts*, ASM Int, 1996 isbn-10:0871705662.