# **Original Paper**

# Practical IR extinction coefficients for water in commercial glasses determined by nuclear reaction analysis<sup>1)</sup>

#### Stamenko Ilievski

Gesellschaft für Schwerionenforschung, Darmstadt (Germany) and Institut für Kernphysik, Johann Wolfgang Goethe-Universität, Frankfurt/M. (Germany)

Oliver Dersch, Stefan Kinkel, Joachim Maldener, Abdelkader Zouine and Friedrich Rauch

Institut für Kernphysik, Johann Wolfgang Goethe-Universität, Frankfurt/M. (Germany)

Rainer Haspel and Fritz W. Krämer Schott Glas, Mainz (Germany)

For a number of commercial glasses with different chemical compositions the water contents were determined by nuclear reaction analysis (NRA) measurements. These results were used to deduce practical extinction coefficients by comparison with the measured IR absorbance values at 2.8  $\mu$ m. For aluminosilicate and television glasses the practical molar extinction coefficients are given for the first time. Practical extinction coefficients are dependent upon glass composition. With increasing basicity of the glasses studied they decrease from 182 to 24 I/(mol cm).

#### Bestimmung der praktischen IR-Extinktionskoeffizienten für Wasser in kommerziellen Gläsern unter Verwendung der Kernreaktionsanalyse

Für eine Anzahl kommerzieller Gläser mit unterschiedlichen chemischen Zusammensetzungen wurden die Wassergehalte unter Verwendung der Kernreaktionsanalyse bestimmt. Diese Werte wurden benutzt, um durch Vergleich mit den gemessenen IR-Absorbanzwerten bei 2.8 µm praktische molare Extinktionskoeffizienten abzuleiten. Für Alumosilicat- und Fernsehgläser werden sie zum erstenmal angegeben. Die praktischen molaren Extinktionskoeffizienten hängen von der Glaszusammensetzung ab und verringern sich mit zunehmender Basizität der untersuchten Gläser von 182 auf 24 l/(mol cm).

### 1. Introduction

Commercial glasses contain small amounts of water (up to 500 wt-ppm in soda-lime-silica glasses [1]) in the form of OH groups, which affect the structure and various properties such as viscosity, index of refraction and heat transfer [2 and 3]. Recently, owing to the rising use of oxy-fuel burners in melting tanks, which leads to higher water contents compared to the traditional heating, there is renewed interest in determining the water content of glasses [4 and 5]. For this purpose the fastest and most convenient method used is IR spectroscopy, by which the strength of the absorption bands caused by OH groups is measured. As shown by Scholze there are three bands at about 2.8, 3.6 and 4.3 µm which are attributed to free, weakly bonded and strongly bonded hy= droxyl groups, respectively [1, 6 and 7]. The water content  $c_{H_{2}O}$  of a glass can be calculated by using the formula

$$c_{\rm H_{2O}} \equiv A_{2.8}/\varepsilon_{2.8} + A_{3.6}/\varepsilon_{3.6} + A_{4.3}/\varepsilon_{4.3} , \qquad (1)$$

where the  $A_i$  are the measured absorbances and the  $\varepsilon_i$  are the extinction coefficients for the three bands. Because of difficulties in measuring the band at 4.3 µm, Scholze introduced the so-called two-band method. The water content is obtained by using the formula

$$c_{\rm H_{2}O} = A_{2.8}/\varepsilon_{2.8} + 4/3 A_{3.6}/\varepsilon_{3.6} , \qquad (2)$$

in which the factor 4/3 takes into account the empirical ratio  $A_{3,6}/A_{4,3} \approx 3$ . Evidently, the  $\varepsilon_i$  have to be known and, thus, the IR measurements have to rely on other measuring techniques which deliver these parameters.

In a more simplified procedure, suggested by Scholze originally for soda-lime-silica glasses [6], a so-called practical molar extinction coefficient  $\varepsilon_{\text{pract}}$  is introduced, which relates the total water content to the absorbance at the 2.8 µm band, given by the formula

$$c_{\rm H_2O} \equiv A_{2.8}/\varepsilon_{\rm pract} \ . \tag{3}$$

Received 10 March, revised manuscript 30 August 1999. <sup>1)</sup> Presented in parts in German at: 71<sup>st</sup> Annual Meeting of the German Society of Glass Technology (DGG) in Bayreuth (Germany) on 28 May 1997.

According to this so-called single-band method, which is commonly used in the glass industry, the total water content can be obtained by analysing only this particular absorbance band. This method has the advantage that it can be applied also to glasses containing boron, for which the BO band near 3.6  $\mu$ m masks the OH band at this wavelength. Again,  $\varepsilon_{\text{pract}}$  has to be known for calculating  $c_{\text{H}_2\text{O}}$  from the measured value of  $A_{2.8}$ :

Extinction coefficients have been determined in the past mostly by using hot extraction methods and also by using nuclear magnetic resonance (NMR). Recently, nuclear reaction analysis (NRA) was introduced as a further method for measuring absolute water concentration values [8]. By using the NRA method the hydrogen concentration  $c_{\rm H}$  of a sample is measured. For low water contents of a glass (< 1000 wt-ppm H<sub>2</sub>O), when water is dissolved as OH and the presence of molecular water normally is excluded [9],  $c_{\rm H}$  is equivalent to the OH concentration.

In the present study, this method was applied to a number of multi-component technical and optical glasses with a large range of different chemical compositions. The results were combined with those from IR spectroscopy to deduce practical extinction coefficients for these glasses.

### 2. Experimental

# 2.1 Glasses and sample preparation

Mainly production-type glasses - optical and technical glasses - were investigated. They are listed in table 1, which shows for each glass the producer/supplier, the trade mark/type, the code number and the main components. Also listed are the basicity numbers B, calculated according to the glass composition [10], which will be used in section 3. They have uncertainties up to 10% for soda-lime-silica glasses and up to 20% for aluminosilicate and lead-silicate glasses as unknown fractions of network formers, intermediates and modifiers in different coordination numbers influence the specific basicity weighting factors of oxides, and thus the basicity of the glass. The B value of the lead-borate glass is not given because its uncertainty is too large. The samples were prepared in the form of thin plates with polished surfaces. The thicknesses varied between 0.5 and 2 mm.

#### 2.2 NRA measurements

The NRA measurements were performed using the <sup>15</sup>N technique. This technique is based on the resonant nuclear reaction <sup>1</sup>H(<sup>15</sup>N, $\alpha\gamma$ )<sup>12</sup>C and measures the hydrogen concentration in a material independent of the type of chemical bonding. The hydrogen concentration versus depth (hydrogen depth profile) in a sample is obtained by measuring the yield of the characteristic  $\gamma$ -rays ( $E_{\gamma} = 4.43$  MeV) versus the <sup>15</sup>N ion beam energy, which is increased stepwise, beginning at the resonance energy (6.385 MeV).

The measuring set-up used for the present study provides a sensitivity of about 10 at.-ppm hydrogen [11]. A polymer foil of known hydrogen content (Kapton<sup>®</sup>) was used as reference standard for determining the detection efficiency of the set-up. As known from previous experiments, some materials, in particular polymers, lose hydrogen under <sup>15</sup>N bombardment. Therefore, to obtain the true yield it was necessary to do repeated measurements on the reference with small ion doses and to extrapolate the measured signal yield to dose zero. The behaviour of the  $\gamma$ -ray yield under ion bombardment was also examined for the glass samples, and it was found that no hydrogen loss occured.

The beam energy range covered in the profiling measurements was in most cases between 6.4 and 10 MeV, corresponding to a depth range of about 2  $\mu$ m. The conversion from beam energy to depth varies somewhat from glass to glass, depending on the composition and on the density of the glass. A representative hydrogen depth profile is shown in figure 1. Near the surface some high-lying data points are indicative of a hydration layer, otherwise the profile is basically flat, as expected for a uniform hydrogen concentration in the bulk. The scatter of the data points is due to counting statistics.

In order to obtain the bulk hydrogen concentration value  $c_{\rm H}$  of a given glass, the data points of the profile were averaged, excluding those of the hydration layer. Most of the samples were profiled two or three times in order to improve the statistical accuracy. This was necessary in particular when the samples showed a rather wide hydration layer (sometimes extending to several 100 nm) which reduced the useful depth range.

For several of the glasses containing boron or lithium, the energy range (and hence the depth range) for averaging did not extend to 10 MeV because of background  $\gamma$ -radiation from nuclear reactions between the <sup>15</sup>N projectiles and boron or lithium target nuclei. Owing to the energy dependence of the cross section of these reactions, the background yield increases roughly exponentially with the <sup>15</sup>N beam energy. Therefore, it may become much larger above a certain energy than the  $\gamma$ -ray yield from hydrogen, depending on the hydrogen content and the boron or lithium content of the glass.

This effect is illustrated by the hydrogen depth profile in figure 2. There is a flat region useful for averaging which extends only from about 300 to about 1000 nm. The width of this region can be increased to a depth of about 1600 nm by a background correction procedure. For higher energies the statistical error of corrected data points becomes too large. By repeated profiling measurements it was possible to compensate for the limitation in accuracy caused by the background effect.

The  $c_{\rm H}$  values obtained have typical errors between 10 and 20%. They arise in part from the common error of the efficiency calibration (8%) and in part from the statistical error of the average over data points in the profiles of the individual glasses.

Practical IR extinction coefficients for water in commercial glasses determined by nuclear reaction analysis

Table 1. Investigated glasses				
producer/ supplier	trade mark/ glass type	code no.	main components in wt% (rounded)	basicity number <sup>4)</sup>
Heraeus	Suprasil 1 Suprasil 2 Suprasil 311 Herasil		100 SiO <sub>2</sub> 100 SiO <sub>2</sub> 100 SiO <sub>2</sub> 100 SiO <sub>2</sub>	13 13 13 13
Schott	Suprax Duran Duran Fiolax klar Ceran AF45 H4 TV glass TV glass BK 7 SF 1 LF 5 KzFS 1 FK 3	8486 8330 8329 8412 85750 8252 8055 8056	79 SiO <sub>2</sub> , 13 B <sub>2</sub> O <sub>3</sub> , 3 Al <sub>2</sub> O <sub>3</sub> , 2 BaO, 1 CaO 81 SiO <sub>2</sub> , 13 B <sub>2</sub> O <sub>3</sub> , 3 Na <sub>2</sub> O, 1 K <sub>2</sub> O, 2 Al <sub>2</sub> O <sub>3</sub> 81 SiO <sub>2</sub> , 13 B <sub>2</sub> O <sub>3</sub> , 2 Na <sub>2</sub> O, 2 Al <sub>2</sub> O <sub>3</sub> 75 SiO <sub>2</sub> , 10 B <sub>2</sub> O <sub>3</sub> , 7 Na <sub>2</sub> O, 5 Al <sub>2</sub> O <sub>3</sub> , 1 CaO 64 SiO <sub>2</sub> , 23 Al <sub>2</sub> O <sub>3</sub> , 4 Li <sub>2</sub> O, 2 BaO, 2 ZnO, 2 ZrO <sub>2</sub> , 2 TiO <sub>2</sub> 50 SiO <sub>2</sub> , 14 B <sub>2</sub> O <sub>3</sub> , 12 Al <sub>2</sub> O <sub>3</sub> , 24 BaO 60 SiO <sub>2</sub> , 4 B <sub>2</sub> O <sub>3</sub> , 14 Al <sub>2</sub> O <sub>3</sub> , 9 BaO, 10 CaO, 2 MgO 61 SiO <sub>2</sub> , 8 Na <sub>2</sub> O, 8 K <sub>2</sub> O, 9 SrO, 10 BaO, 2 Al <sub>2</sub> O <sub>3</sub> , 1 ZrO <sub>2</sub> 60 SiO <sub>2</sub> , 8 Na <sub>2</sub> O, 7 K <sub>2</sub> O, 9 SrO, 10 BaO, 4 Al <sub>2</sub> O <sub>3</sub> , 1 ZrO <sub>2</sub> 70 SiO <sub>2</sub> , 11 B <sub>2</sub> O <sub>3</sub> , 10 Na <sub>2</sub> O, 6 K <sub>2</sub> O, 2 BaO 30 SiO <sub>2</sub> , 8 Na <sub>2</sub> O, 5 K <sub>2</sub> O, 57 PbO 52 SiO <sub>2</sub> , 6 Na <sub>2</sub> O, 8 K <sub>2</sub> O, 34 PbO 53 B <sub>2</sub> O <sub>3</sub> , 15 Al <sub>2</sub> O <sub>3</sub> , 3 Na <sub>2</sub> O, 7 Al <sub>2</sub> O <sub>3</sub> , 10 K <sub>2</sub> O, 6 F <sub>2</sub>	15 15 14 20 25 21 29 35 35 25 26 25 20
TNO <sup>2)</sup>	container glass A container glass B		72 SiO <sub>2</sub> , 14 Na <sub>2</sub> O, 14 (CaO, MgO) 73 SiO <sub>2</sub> , 14 Na <sub>2</sub> O, 13 (CaO, MgO)	35 35
Saint Gobain <sup>3)</sup>	S.G. clear glass S.G. amber glass		71 SiO <sub>2</sub> , 14 Na <sub>2</sub> O, 10 CaO, 4 MgO 71 SiO <sub>2</sub> , 14 Na <sub>2</sub> O, 11 CaO, 4 MgO	37 36
DGG	Standard glass II		72 SiO <sub>2</sub> , 14 Na <sub>2</sub> O, 10 CaO, 3 MgO	36
unknown supplier	float glass		71 SiO <sub>2</sub> , 15 Na <sub>2</sub> O, 10 CaO, 4 MgO	37

<sup>2)</sup> Round robin test samples TC14 of ICG delivered by TNO Institute of Applied Physics.

<sup>3)</sup> Round robin test samples TC14 of ICG delivered by Saint Gobain Recherche.

<sup>4)</sup> According to [10], with an acid value of 90 for  $Al_2O_3$ .



Figure 1. Hydrogen depth profile of the glass 8055. The line indicates the depth range that was used for averaging.

# 2.3 IR spectroscopy measurements

The IR spectroscopy measurements were performed using a Perkin Elmer spectrometer (Mod. 682). The spectra covered the wave number range 4000 to  $2000 \text{ cm}^{-1}$ . As examples, in figure 3 the spectra of a silica glass (Suprasil 1), of an optical lead-silicate glass (SF 1), of a technical borosilicate glass (8330) and of a technical soda-lime-silica glass (float glass) are shown.



Figure 2. Hydrogen depth profile of the glass BK 7, before ( $\bullet$ ) and after ( $\bigcirc$ ) correction for boron background. The line indicates the depth range that was used for averaging.

Comparison of the spectra of samples with different thicknesses from a given glass showed that water absorbed at the sample surface or in a hydrated layer had no influence on measured absorbance values. For each spectrum two transmittance values,  $T_{2.5}$  and  $T_{2.8}$ , were determined from which  $A_{2.8}$  was deduced according to

$$A_{2.8} = \lg(T_{2.5}/T_{2.8})/d , \qquad (4)$$

#### Stamenko Ilievski et al.:



Figure 3. Infrared spectral transmittance of different glass types; spectrum 1: vitreous silica (Suprasil 1); spectrum 2: optical glass (SF 1); spectrum 3: borosilicate glass (Duran no. 8330); spectrum 4: soda-lime-silica glass (float glass).

where *d* is the sample thickness,  $T_{2.5}$  is the value at  $\lambda = 2.5 \,\mu\text{m}$ , where absorption due to OH groups does not take place, and  $T_{2.8}$  is the value at the absorption minimum arising from the 2.8 µm band. In reality, the position of the minimum is not exactly 2.8 µm and varies somewhat from glass to glass. The accuracy of the absorbance values is within 5% comprising errors from thickness and transmittance measurements. It should be noticed that the accuracy of the absorbance will be reduced in the rare case of a high iron-containing glass (FeO > 5000 wt-ppm) because the spectral transmittance in the range between 2.5 and 3.6 µm is affected by the tail of the broadband near IR absorption of ferrous iron [12].

### 3. Results and discussion

The results of the NRA measurements are listed in the second column of table 2 as hydrogen concentration values  $c_{\rm H}$  in units of at.-ppm. Thus,  $c_{\rm H}$  denotes the number of hydrogen atoms among 10<sup>6</sup> atoms of all the elements forming the glass. For example, 800 at.-ppm hydrogen in SiO<sub>2</sub> means 800 hydrogen atoms and 999200 silicon and oxygen atoms. The corresponding H<sub>2</sub>O weight fractions, in units of wt-ppm, are given in column 3. Using the respective density values of the glasses, they were converted into the values for the water concentration in units of mmol H<sub>2</sub>O/l, listed in column 4.

From these concentration values and the absorbance values, given in column 5, the practical molar extinction coefficients of the glasses (column 6) were calculated according to equation 3. Their errors are mainly determined by the errors of the  $c_{\rm H}$  values, since the errors of the A values are comparatively small.

Furthermore, in table 3 the water contents and extinction coefficients are listed separately for the different glass types. The values of  $\varepsilon_{\text{pract}}$  between 44 and 55 l/(mol cm) for important industrial soda-lime-silica

glasses agree reasonably well with the corresponding literature values [13]. Also the extinction coefficients for vitreous silica between 137 and 182 l/(mol cm) are in accordance with a recent compilation [14] taking into account that  $\varepsilon_{H_2O} = 2 \cdot \varepsilon_{OH}$ : In contrast to this the values found by Williams et al. [13] for vitreous silica and for technical borosilicate glasses are by a factor  $\approx 2$  smaller than those cited in [14] and those of the present paper. For technical aluminosilicate and television glasses no extinction coefficients are known until now. Therefore, the present values (table 3) may be regarded as keystones for determining the water content of these glasses by IR measurements.

#### 3.1 Water content

As can be seen in table 2 the water contents of the various glasses differ considerably, ranging from about 5 to 200 mmol/l. In general it will be difficult to isolate the different parameters influencing the water content. However, the observation that, under usual melting conditions, the lead-borate and boro-silica glasses have the highest water content, see tables 2 and 3, can probably be attributed to the ability of boron to form water-rich compounds.

Also the influence of the melting conditions, which are now coming into interest when using oxy-fuel burners for melting production glasses, can be clearly seen. For instance, in spite of the same glass composition, the oxy-fuel melted container glass A has a water content 50% higher than that of the air-fuel melted container glass B. This is due to the higher water content of the gas atmosphere in the melting tank when oxy-fuel fired. Another example is provided by glass type 8329 which has nearly the same composition as glass type 8330 but, in contrast to that, is melted under low pressure. Therefore, it is to a large extent degassed and has a water content more than one decade lower compared with glass type 8330. The differences between various kinds of silica glass can also be understood as a result of different melting conditions [15].

## 3.2 Practical molar extinction coefficient

As mentioned above, Scholze introduced two methods to deduce the water content from IR transmittance measurements, the two-band method and the singleband method. With regard to the two-band method the molar extinction coefficients were determined by Scholze as  $\varepsilon_{2.8} = 70 \text{ l/(mol cm)}$  and  $\varepsilon_{3.6} = 150 \text{ l/(mol cm)}$ for a range of soda-lime-silica glasses, and these values were widely accepted subsequently. That is why ICG technical committee TC14 "Gases in Glass" adopted his method and with a specific evaluation of the transmittance curves gave a recommended procedure for the IR spectroscopic determination of water in soda-lime-silica glasses [16]. Recently, similar values were obtained by Harder et al. [17] for soda-lime-, potassium-lime- and Practical IR extinction coefficients for water in commercial glasses determined by nuclear reaction analysis

	F			8	
glass type/trade mark/code no.	$c_{\rm H}$ in atppm	$c_{\rm H_{2O}}$ in wt-ppm	$c_{\rm H_2O}$ in mmol H <sub>2</sub> O/l	A in cm <sup>-1</sup>	$\varepsilon_{\rm pract}$ in l/(mol cm)
Suprasil 1	860	385	47	8.2	175 ± 17
Suprasil 2	800	360	44	8.0	$182 \pm 18$
Suprasil 311	300	140	17	2.7	$156 \pm 20$
Herasil	240	106	13	1.8	$137 \pm 21$
Suprax	700	318	41	3.5	$85 \pm 17$
Duran 8330	1300	616	76	7	$93 \pm 14$
Duran 8329	80	36	4.6	0.5	$120 \pm 24$
Fiolax klar	1270	580	77	5.9	$76 \pm 9$
Ceran <sup>5)</sup>	800	355	49	3.6	$74 \pm 15$
Ceran <sup>5)</sup>	600	270	37	2.7	$72 \pm 14$
AF 45	830	330	50	3.9	$80 \pm 10$
H4	510	212	31	2.4	77 ± 9
TV glass 8055	810	305	47	1.5	$31 \pm 5$
TV glass 8056	830	310	48	1.4	$30 \pm 5$
BK 7	1100	475	66	3.5	$50 \pm 8$
SF 1	810	186	46	2.3	$50 \pm 6$
LF 5	640	202	36	0.9	$24 \pm 3$
KzFS 1	2600	1150	200	17.6	88 ± 13
FK 3	730	246	31	4.5	$106 \pm 21$
container glass A	1200	518	72	3.2	$45 \pm 5$
container glass B	800	346	48	2.1	44 ± 5
S.G. clear glass	620	266	37	2	$55 \pm 7$
S.G. amber glass	540	240	33	1.7	$50 \pm 6$
DGG Standard glass II	630	275	38	1.8	$48 \pm 6$
float glass	560	242	33	1.9	$55 \pm 7$

Table 2. NRA and IR results and deduced practical extinction coefficient of the different glasses

<sup>5)</sup> Produced on different days.

Table 3.	Water	content	and	practical	extinction	coefficient	of
different	glass t	ypes					

glass type (conventionally produced)	water content in mmol/l	practical extinction coefficient in l/(mol cm)
lead-borate glass	200	88
borosilicate glass	41 to 77	76 to 93
television glass	47 to 48	30 to 31
aluminosilicate glass	31 to 50	72 to 80
soda-lime-silica glass	33 to 48	44 to 55
silica glass	13 to 47	137 to 182

Table 4. Ratio of absorbances for the 2.8 and 3.6  $\mu$ m bands and  $\varepsilon_{\text{pract}}$  values for some of the glasses studied

glass	$A_{2.8}/A_{3.6}$	€ <sub>pract</sub>
LF 5	0.32	24
TV glass 8055	0.47	31
TV glass 8056	0.49	30
SF 1	0.74	50
DGG Standard glass II	0.84	48
S.G. clear glass	0.94	55
S.G. amber glass	0.95	50
float glass	0.98	55
container glass A	1.08	45
container glass B	1.02	44

caesium-lime-silicate model glasses ( $16R_2O \cdot 10CaO \cdot 74SiO_2$ ), with values of  $\varepsilon_{2.8} = 76 l/(mol cm)$  and  $\varepsilon_{3.6} = 164 l/(mol cm)$ .

Concerning the single-band method, Scholze proposed a practical molar extinction coefficient of 41 l/ (mol cm), valid only for simple soda-lime-silica glasses. In later years this value, or sometimes 40 l/(mol cm), was applied in the glass industry for all types of glass, although there is no justification. According to Scholze's results for model glasses,  $\varepsilon_{\text{pract}}$  should depend at least upon the alkali and alkaline earth content of the glasses since it influences the relative amounts of free, weakly bonded and strongly bonded OH groups, and one might expect that additional factors play a role. Indeed, as was reported in [13] the extinction coefficient for the 2.8 µm band of eight glasses varied distinctly with the glass

composition. The large variability of  $\varepsilon_{\text{pract}}$  is confirmed by the present results with values between 24 and 182 l/ (mol cm).

For some of the glasses studied for which the 2.8 and 3.6 µm bands were distinguishable in the IR spectra, the ratio  $A_{2.8}/A_{3.6} = \lg(T_{2.5}/T_{2.8})/\lg(T_{2.5}/T_{3.6})$  could be deduced. This ratio is a measure for the relative amounts of free and weakly bonded OH groups provided that  $\varepsilon_{2.8}$  and  $\varepsilon_{3.6}$  are universal for silicate glasses (compare equation (1)), see also [18]. Table 4 shows this ratio together with the  $\varepsilon_{\text{pract}}$  values of these glasses. As can be seen there is a fair correlation between these quantities:  $\varepsilon_{\text{pract}}$  decreases with decreasing ratio  $A_{2.8}/A_{3.6}$ . This means that, under the above assumption, the decrease of  $\varepsilon_{\text{pract}}$  indicates a decreasing fraction of free OH groups. It ap-



Figure 4. Plot of the practical extinction coefficient versus the sum of alkali and alkaline earth oxides.



Figure 5. Plot of the practical extinction coefficient versus the basicity number. The solid line (middle) is described by the function  $\varepsilon(B) = 2660 - B^{-1.15} \text{ l/(mol cm)}$ ; the dashed lines are given by the functions  $\varepsilon(B) \pm 35 \%$ .

pears likely that also for other glasses the  $\varepsilon_{\text{pract}}$  value is determined at least partly by the fraction of free OH groups.

It would be most useful for the industrial practice if a simple dependence of  $\varepsilon_{\text{pract}}$  on an easily accessible parameter could be found so that the  $\varepsilon_{\text{pract}}$  values of further glasses could be estimated. As such a parameter the sum of the alkali and alkaline earth components comes into question. It can be seen in figure 4 that there is indeed a trend of  $\varepsilon_{\text{pract}}$  decreasing with increasing amount of these components; however, the data points show a large scatter.

Another parameter to be considered is the basicity of the glasses which should in principle be a better parameter. As discussed by Scholze the portion of dissolved water attributed to the 2.8  $\mu$ m band depends on the type of network modifiers [7]. Thus  $e_{\text{pract}}$  should be a function of the basicity number *B* which takes into account both the concentrations and the field strengths

glass type	ε <sub>pract</sub> in l/(mol cm)	basicity number
soda-lime-silica	$38 \pm 3$	34
potassium-lime-silicate	$23 \pm 2$	35
caesium-lime-silicate	$21 \pm 2$	36

of the modifiers, intermediates and network formers [10]. Therefore, in figure 5 the  $\varepsilon_{\text{pract}}$  values of this study are plotted against *B*. One recognizes a distinct dependence although the scatter of the data points is similar to that in figure 4. Still, based on the data in figure 5 it can be stated that, in general, the higher the basicity of the glass, the lower the practical extinction coefficient. The following empirical relation between the extinction coefficients and the *B* values is obtained by least-squares fit

$$\varepsilon(B) \equiv 2660 : B^{-1.15} \, \text{l/(mol cm)}.$$
 (5)

All determined  $\varepsilon_{\text{pract}}$  values, with exception of the value for glass LF 5, are lying within a band described by  $\varepsilon(B) \pm 35\%$ . Furthermore, the values of Williams et al. [13] for soda-lime-silica glass and those for silica glass [14] are within this band. This also holds approximately for the above mentioned model glasses [8 and 17] as seen in table 5. Thus, one can use relation (5) to estimate the practical extinction coefficient of other commercial glasses from their basicity numbers.

#### 4. Conclusion

Practical molar extinction coefficients  $\varepsilon_{\text{pract}}$  have been determined for 25 commercial glasses by combining IR spectroscopy with nuclear reaction analysis. For sodalime-silica glasses and vitreous silica the values found here agree reasonably well with literature data but disagree for boron-silicate glasses; for aluminosilicate and television glasses the  $\varepsilon_{\text{pract}}$  values are given for the first time. The values found vary by almost an order of magnitude. With increasing contents of alkali and alkaline earth components and with increasing basicity, Epract decreases from 182 to 24 l/(mol cm). An equation for estimating  $\varepsilon_{\text{pract}}$  for other glasses from the basicity number is given. With the assumption that the extinction coefficients for the two bands at 2.8 and 3.6  $\mu$ m are universal for silicate glasses, the decrease of  $\varepsilon_{\text{pract}}$  mentioned can be attributed in part to a decrease of the fraction of free OH groups.

#### 5. References

- [1] Scholze, H.: Glas Natur, Struktur und Eigenschaften. 3rd ed. Berlin et al.: Springer, 1988.
- [2] Fenstermacher, J. E.; Lesser, R. C.; Ryder, R. J.: A study of water content of container glasses. Glass Ind. 46 (1965) no. 9, p. 518-521.

- [3] Brückner, R.; Hessenkemper, H.: Influence of water content and basicity on redox ratio – consequences on radiation heat absorption and emission of glass melts during fining and processing. Glastech. Ber. 66 (1993) no. 10, p. 245-253.
- [4] Beerkens, R.; Laimböck, P.; Kobayashi, H.: The effect of water on fining, foaming and redox of sulfate containing glass melts. In: Clare, A. G.; Jones, L. E. (eds.): Advances in fusion and processing of glass II. Proc. 5th Int. Sym. Advances in Fusion and Processing of Glass, Toronto 1997. Westerville, OH: Am. Ceram. Soc., 1998. p. 43–49 (Ceram. Trans. Vol. 82.)
- [5] Kobayashi, H.; Beerkens, R. G. C.: Reduction of SO<sub>2</sub> emissions with oxy-fuel firing "Water enhanced sulfate fining". In: Clare, A. G.; Jones, L. E. (eds.): Advances in fusion and processing of glass II. Proc. 5th Int. Sym. Advances in Fusion and Processing of Glass, Toronto 1997. Westerville, OH: Am. Ceram. Soc., 1998. p. 57–64 (Ceram. Trans. Vol. 82.)
- [6] Scholze, H.: Der Einbau des Wassers in Gläsern. I. Der Einfluß des im Glas gelösten Wassers auf das Ultrarot-Spektrum und die quantitative ultrarotspektroskopische Bestimmung des Wassers in Gläsern. Glastechn. Ber. 32 (1959) no. 3, p. 81–88.
- [7] Scholze, H.: Der Einbau des Wassers in Gläsern. II. UR-Messungen an Silikatgläsern mit systematisch variierter Zusammensetzung und Deutung der OH-Banden in Silikatgläsern. Glastechn. Ber. 32 (1959) no. 4, p. 142–152.
- [8] Harder, U.; Geißler, H.; Gaber, M. et al.: Determination of the water content of alkali lime silica glasses by IR spectroscopy using nuclear reaction analysis for calibration. Glastech. Ber. Glass Sci. Technol. 71 (1998) no. 1, p. 12-18.
- [9] Zarzycki, J.: Le verre et l'eau. Riv. Stn. Sper. Vetro (1984) no. 5, p. 17–28.

- [10] Krämer, F. W.: Contribution to basicity of technical glass melts in relation to redox equilibria and gas solubilities. Glastech. Ber. 64 (1991) no. 3., p. 71-80.
- [11] Endisch, D.; Sturm, H.; Rauch, F.: Nuclear reaction analysis of hydrogen at levels below 10 atom.ppm. Nucl. Instr. Meth. B 84 (1994) p. 380-392.
- [12] Boulos, E. N.; Glebov, L. B.; Smirnova, T. V.: Absorption of iron and water in the Na<sub>2</sub>O-CaO-MgO-SiO<sub>2</sub> glasses. I. Separation of ferrous and hydroxyl spectra in the near IR region. J. Non-Chryst. Solids **221** (1997) p. 213–221.
- [13] Williams, J. P.; Su, Y.-S.; Strzegowski, W. R. et al.: Direct determination of water in glass. Am. Ceram. Soc. Bull 55 (1976) no. 5, p. 524–527.
- [14] Davis, K. M.; Agarwal, A.; Tomozawa, M. et al.: Quantitative infrared spectroscopic measurement of hydoxyl concentrations in silica glass. J. Non-Cryst. Solids 203 (1996) p. 27–36.
- [15] Witzke, H.-D.: Some new studies on the outgassing and dehydroxylisation of different kinds of fused quartz by high temperatures. Glastech. Ber. 63 K (1990) p. 333-341.
- [16] Geotti-Bianchini, F.; Geißler, H.; Krämer, F. et al.: 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". Glastech. Ber. Glass Sci. Technol. **72** (1999) p. 103–111.
- [17] Harder, U.; Geißler, H.: IR spectroscopic investigations on the determination of the water content in glasses. Fresenius J. Anal. Chem. 361 (1998) p. 585-586.
- [18] Geotti-Bianchini, F.; de Riu, L.: Infrared spectroscopic analysis of water incorporated in the structure of industrial soda-lime-silica glasses. Glastech. Ber. Glass Sci. Technol. 68 (1995) no. 7, p. 228-240.

0200P002

Addresses of the authors:

S. Ilievski KP II Gesellschaft für Schwerionenforschung Planckstraße 1 D-64291 Darmstadt

O. Dersch, S. Kinkel, J. Maldener, A. Zouine, F. Rauch Institut für Kernphysik Johann Wolfgang Goethe Universität August-Euler-Straße 6 D-60486 Frankfurt am Main

R. Haspel, F. W. Krämer Schott Glas Hattenbergstraße 10 D-55122 Mainz