

## Determination of the water content of alkali lime silica glasses by IR spectroscopy using nuclear reaction analysis for calibration<sup>1)</sup>

Ulrike Harder, Heinz Geißler, Martin Gaber and Manfred Hähner  
Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin (Germany)

Oliver Dersch and Friedrich Rauch  
Institut für Kernphysik, Johann-Wolfgang-Goethe-Universität, Frankfurt/M. (Germany)

Dedicated to Prof. Dr. Helmut A. Schaeffer on the occasion of his 60th birthday

---

Systematic IR and NRA investigations were performed for two series of glasses with very different water contents. The glasses had the composition (in mol%):  $16 R_2O \cdot 10 CaO \cdot 74 SiO_2$  ( $R =$  sodium, potassium). The IR absorption coefficients of the OH bands were found to be linearly correlated with the total hydrogen content obtained by the NRA measurements. Using the hydrogen concentration values from NRA, the total water contents were calculated and so-called practical IR extinction coefficients were deduced. The values found for the soda-lime-silica glasses are  $381 \cdot mol^{-1} \cdot cm^{-1}$  for the band at  $3550 cm^{-1}$  and  $561 \cdot mol^{-1} \cdot cm^{-1}$  for the band at  $2800 cm^{-1}$ . The values for the potassium-lime-silica glasses are  $231 \cdot mol^{-1} \cdot cm^{-1}$  for the band at  $3550 cm^{-1}$  and  $781 \cdot mol^{-1} \cdot cm^{-1}$  for the band at  $2800 cm^{-1}$ . Also, Scholze's two-band method was applied, resulting in good agreement between the water contents of the glasses derived from the IR and the NRA measurements.

### Bestimmung des Wassergehaltes von Alkali-Kalksilicatgläsern mittels IR-Spektroskopie unter Verwendung der Kernreaktionsanalyse zur Kalibrierung

An zwei Serien von Gläsern der Zusammensetzung (Stoffmengenanteil in %):  $16 R_2O \cdot 10 CaO \cdot 74 SiO_2$  ( $R =$  Natrium, Kalium) mit sehr unterschiedlichen Wassergehalten wurden systematische IR- und NRA-Untersuchungen durchgeführt. Es wurde ein linearer Zusammenhang zwischen den IR-Absorptionskoeffizienten der OH-Banden und dem mittels NRA-Messungen erhaltenen absoluten Wasserstoffgehalt gefunden. Aus den mit der NRA bestimmten absoluten Wasserstoffkonzentrationen wurden die Gesamtwassergehalte berechnet und zur Bestimmung der sogenannten praktischen Extinktionskoeffizienten verwendet. Für Natron-Kalksilicatgläser wurden die Werte  $381 \cdot mol^{-1} \cdot cm^{-1}$  für die Bande bei  $3550 cm^{-1}$  und  $561 \cdot mol^{-1} \cdot cm^{-1}$  für die Bande bei  $2800 cm^{-1}$  ermittelt. Die entsprechenden Werte für Kali-Kalksilicatgläser betragen  $231 \cdot mol^{-1} \cdot cm^{-1}$  für die Bande bei  $3550 cm^{-1}$  bzw.  $781 \cdot mol^{-1} \cdot cm^{-1}$  für die Bande bei  $2800 cm^{-1}$ . Zusätzlich wurde die Zwei-Banden-Methode nach Scholze angewendet. Die damit erhaltenen Wassergehalte der Gläser stimmen gut mit den entsprechenden aus den NRA-Messungen abgeleiteten Wassergehalten überein.

---

## 1. Introduction

Nearly all types of commercial glasses contain a certain amount of water. The term "water", as used here, includes molecular, more or less associated water as well as bound water in form of silanol groups. The structure and many properties of silicate glasses sensitively depend on the water content. The water content is e.g. of special interest for optical glasses. Besides optical and infrared properties, also the viscosity and thus the ability to be processed, the formation of bubbles as well as the tendency to separate into different phases, and the tendency to crystallize depend on the insertion of water into the glass network. Also bubble defects and heat balance within the melt are touched. Prerequisite for the techno-

logical mastery of the problems mentioned is fundamental knowledge of structural insertion of water into glasses.

IR spectroscopy is a very fast, inexpensive and convenient method for determination of water contents in glasses. But the results are only relative ones. The water contents of various glasses can be compared accurately, but the absolute water content cannot be determined without calibration [1]. Methods used for calibration of IR spectroscopic results are for example vacuum hot extraction (VHE) or gas bubbling with subsequent quantitative water analysis by gravimetric methods [2 to 5], mass spectroscopy [4, 6 and 7], measurements of vapour pressure [8 to 10], NMR spectroscopy [11 to 15], or other methods.

As an alternative method, nuclear reaction analysis (NRA) should be suitable. The objective of the present work is to examine the practical usefulness of NRA for obtaining a calibration. Nuclear interactions are insensi-

---

Received July 11, 1997.

<sup>1)</sup> Presented in German at: 71st Annual Meeting of the German Society of Glass Technology (DGG) on May 28, 1997 in Bayreuth (Germany).

Table 1. Description of the glass samples

	glass no.	sample description
SLS glasses	1	nitrogen-dried
	2	nitrogen-dried
	3	basic glass
	4	water-enriched glass with bubbles
	5	water-enriched
PLS glasses	6	nitrogen-dried
	7	nitrogen-dried
	8	basic glass
	9	water-enriched

tive to the kind of chemical binding in a sample. This means in the present context that the total hydrogen content in a glass sample is measured, independent of its distribution over different types of OH bondings. The NRA method utilized here is the  $^{15}\text{N}$  technique; pertinent examples of its application are the determination of the hydrogen content of thin films [16 and 17] and of minerals [18 and 19] and the study of glass/water interactions [20 and 21]. The  $^{15}\text{N}$  technique is a very sensitive and non-destructive working method; however, it requires a relatively high expenditure of equipment. A necessary condition for the applicability of NRA for calibration of IR extinction coefficients is that all hydrogen in the materials belongs to the hydroxyl groups. This condition is fulfilled for the glasses studied here.

## 2. Experimental

### 2.1 Glass preparation

A soda–lime–silica (SLS) glass and a potassium–lime–silica (PLS) glass with the composition (in mol%)  $16\text{R}_2\text{O} \cdot 10\text{CaO} \cdot 74\text{SiO}_2$ , R = sodium, potassium, were prepared. The glasses were molten from raw materials in a platinum crucible in an induction furnace at  $1500^\circ\text{C}$ . The water content of the basic glasses was below 0.05 mass%. The basic glasses were treated in various ways in order to get two series of glasses of different water content (table 1). A part of the basic glasses was dried by nitrogen bubbling through the glass melt, another part was enriched with water by bubbling with steam. The exact conditions of glass melting and glass treatment and a scheme of the apparatus for the different treatments are published in [7]. For the IR spectroscopic investigations, the glasses were prepared into thin plates of various thicknesses (0.3 to 10 mm) and water-free polished on both sides.

### 2.2 Infrared spectroscopic measurements

The measurements were carried out on the FTIR vacuum spectrometer IFS 66v (Bruker GmbH, Karlsruhe

(Germany)). The spectra were measured in the wave number region  $4000$  to  $2000\text{ cm}^{-1}$  using the transmission technique. Nearly the whole sample area of about  $10$  to  $100\text{ mm}^2$  was illuminated by the IR beam. Thus, the water concentration deduced from the measurement is the average over the sample. It was shown that the water concentration of the glass samples was proportional to the sample thickness. That means, water adsorbed on the sample surface can be neglected.

Systematic errors of FTIR spectrometers are small (about 2 to 3%). Errors of IR spectroscopic results are more likely caused by sample preparation and sample handling. The homogeneity error was determined by IR microscopy. Deviations from sample homogeneity are below 5% for the glasses investigated. Integration over the sample area led to reduction of homogeneity errors. A special problem concerning errors is the background correction for the glass network (see section 4). The overall error of the  $\text{H}_2\text{O}$  concentration deduced from IR measurements amounts to about 10%.

### 2.3 NRA measurements

The total amount of hydrogen in the glass samples was determined by the  $^{15}\text{N}$  technique which relies on the resonant nuclear reaction  $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ . With this technique the hydrogen concentration versus depth is obtained by measuring the yield of the characteristic  $\gamma$  rays from this reaction versus the beam energy. Depth profiles can be obtained up to a depth of about  $3\text{ }\mu\text{m}$  in glasses. The  $^{15}\text{N}$  measurements were carried out with a low-level set-up for hydrogen analysis which provides a sensitivity of about 10 atom ppm H. The beam current was about 150 nA and the beam spot size was 3 mm in diameter.

Before the measurements, the glass samples were etched in diluted hydrofluoric acid for several minutes in order to remove a possibly existing surface layer containing water incorporated into damage sites arising from the polishing treatment. Two representative hydrogen depth profiles are shown in figure 1. At depths larger than about 500 nm, the profiles are flat indicating that there the hydrogen concentration remains constant. The scatter of the data points is due to counting statistics; statistical errors of single data points were between 7 and 15%. Some of the samples with low hydrogen content were analyzed a second time for improving the statistical accuracy. For obtaining the hydrogen content of a given sample, the data points in the flat region were averaged. This resulted in a statistical error of 3% (6% for the samples with low hydrogen content). Together with a systematic error of about 7%, originating from the uncertainty of the stopping power of the  $^{15}\text{N}$  ions, the overall error of the hydrogen contents is about 9% for all samples.

The unit for water concentrations in glass is usually  $\text{mol} \cdot \text{l}^{-1}$  ( $1\text{ mol} \cdot \text{l}^{-1} \approx 0.72\text{ mass}\%$ ). NRA results are obtained in units of atom ppm H. The conversion factor between atom ppm H and  $\text{mol} \cdot \text{l}^{-1}\text{ H}_2\text{O}$  depends on the

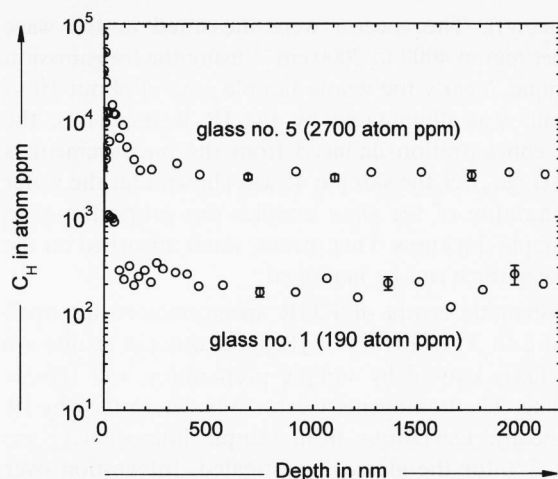


Figure 1. Depth profile of the hydrogen concentration of glass no. 1 (nitrogen-dried) and glass no. 5 (water-enriched) determined by NRA.

molar composition of the glass sample. 1 atom ppm H corresponds to  $6.04 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1} \text{ H}_2\text{O}$  in the case of SLS glasses and to  $5.56 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1} \text{ H}_2\text{O}$  in the case of PLS glasses.

### 3. Determination of water content by IR spectroscopy

The vibrational bands of OH groups are observed in the wave number region between  $4000$  and  $2200 \text{ cm}^{-1}$ . In silicate glasses with water contents below 1 mass%, all water exists in form of silanol groups [22]. The spectra of SLS and PLS glasses contain three different IR bands: at about  $3550$ ,  $2800$  and  $2300 \text{ cm}^{-1}$ . These three bands are characterized by different types of structural insertion of OH groups into the glass network [23]:

- $3550 \text{ cm}^{-1}$ : OH groups in form of silanol, very weakly associated, by Scholze [8]: “free” OH groups;
- $2800 \text{ cm}^{-1}$ : strongly associated OH groups;
- $2300 \text{ cm}^{-1}$ : very strongly associated OH groups, connecting isolated  $\text{SiO}_4$  anions with the glass network.

The water content of the glass samples can be determined from their IR spectra by using the Beer-Lambert law:

$$E = \varepsilon \cdot c \cdot d. \quad (1)$$

In this expression,  $E$  is the extinction (dimensionless),  $d$  is the thickness of the glass sample (in cm),  $c$  is the concentration (in  $\text{mol} \cdot \text{l}^{-1}$ ), and  $\varepsilon$  is the molar extinction coefficient (in  $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ). The product  $\varepsilon \cdot c$  is also called absorption coefficient  $\alpha$  (in  $\text{cm}^{-1}$ ).

$$\alpha = \varepsilon \cdot c = \frac{E}{d}. \quad (2)$$

The extinction coefficient  $\varepsilon$  has to be determined experimentally by calibration using another independent method. According to Scholze [8], there are two different ways to deduce the water concentration of the glass sample from the measured extinctions:

First, the so-called practical extinction coefficient  $\varepsilon_{\text{pract}}(\tilde{\nu})$  is used. In this case, only one of the IR bands has to be evaluated (either the band at  $3550$  or the band at  $2800 \text{ cm}^{-1}$ ). The practical extinction coefficients for SLS glasses for the bands at  $3550$  and  $2800 \text{ cm}^{-1}$  are found in literature (table 2). The use of a practical extinction coefficient implies that the total water content is correlated with the extinction of one IR band. This method will only lead to correct results if the ratio between the IR bands remains constant, in dependence on the water content.

Second, the two-band method by Scholze [8] can be applied. This method considers the band at  $3550$  as well as the band at  $2800 \text{ cm}^{-1}$ . The part of the total water amount which is represented by the first band at  $3550 \text{ cm}^{-1}$  is considered independently from the part represented by the second band at  $2800 \text{ cm}^{-1}$ . The extinction coefficients  $\varepsilon(\tilde{\nu})$  of these two bands used by this method are different from the practical extinction coefficients  $\varepsilon_{\text{pract}}(\tilde{\nu})$ . The part of the water content of the third band is estimated by Scholze to amount to one third of that of the second band so that the total water amount of the glass sample can be determined by the following formula:

$$c_{\text{H}_2\text{O}} = \frac{\alpha_{\text{max}}(\tilde{\nu}_{3550})}{\varepsilon_{3550}} + \frac{\alpha_{\text{max}}(\tilde{\nu}_{2800})}{\varepsilon_{2800}} + \frac{1}{3} \frac{\alpha_{\text{max}}(\tilde{\nu}_{2800})}{\varepsilon_{2800}} \quad (3)$$

with

$$\varepsilon_{2800} = 150 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \text{ and}$$

$$\varepsilon_{3550} = 70 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} [8].$$

In contrast to the use of the practical extinction coefficient, in the case of the two-band method the mutual overlapping of the bands has to be considered. For this reason, band separation has to be carried out. The prerequisite for the applicability of the two-band method to glasses of different composition is that the extinction coefficient for water in glasses depends on the wave number but not on the glass composition. Scholze applied the two-band method to glasses of very different composition with  $\text{SiO}_2$  acting as network former in all cases.

The objective of this work is the determination of practical extinction coefficients for SLS and PLS glasses using NRA for calibration. Besides, the two-band method by Scholze shall be applied to determine the water content of the glasses and to compare them with the water contents determined by NRA.

Table 2. Practical extinction coefficients of this work by calibration with NRA and corresponding values of other authors

		wave number of the IR band in $\text{cm}^{-1}$	$\epsilon_{\text{prakt}}$ in $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$			
			this work	Scholze [8]	Götz [3]	TC14 [24]
SLS glasses	{	3550	38	41	39	40
		2800	56	65	56	—
PLS glasses	{	3550	23	—	—	—
		2800	78	—	—	—

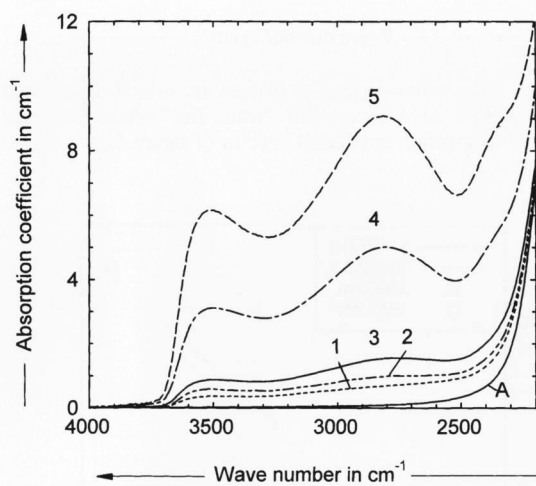


Figure 2. Absorption coefficient spectra of glasses no. 1 to 5 (sample description see table 1) and of a theoretical "water-free" glass A.

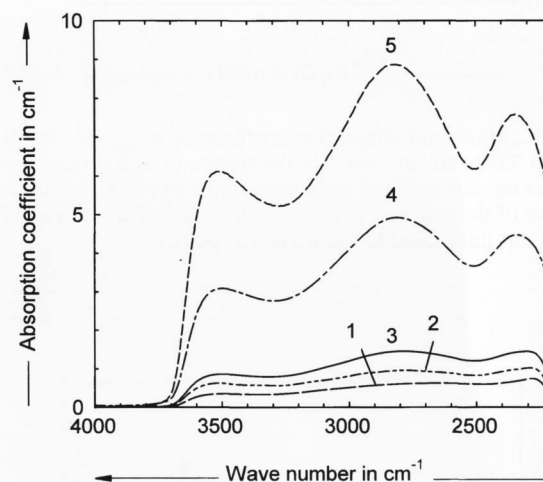


Figure 3. Pure water spectra of glasses no. 1 to 5 determined by subtraction of a theoretical "water-free" glass from the measured absorption coefficient spectra of figure 2.

#### 4. Results and discussion

Figure 2 shows the absorption coefficient spectra of six glasses of the SLS type with different water content. Each of these spectra is a sum spectrum of the glass network spectrum and the water spectrum. In order to determine the water content, the pure water spectrum is needed. O–H bands were mathematically separated from Si–O bands by means of a numerical band separation program. Curve A is obtained as a result of this procedure. It represents the theoretical spectrum of a glass which is absolutely free of OH groups. Difference spectra between curves 1 to 5 and curve A are calculated and plotted in figure 3. The difference spectra of glasses no. 1 to 5 show three bands at 3550, 2800 and 2300  $\text{cm}^{-1}$ . The measured maximum absorption coefficients  $\alpha_{\text{meas}}$  ( $\tilde{\nu} = 3550, 2800 \text{ cm}^{-1}$ ) of the glass samples no. 1 to 5 are summarized in table 3. Additionally, the NRA results of these samples are listed there.

The measured maximum absorption coefficients  $\alpha_{\text{meas}}$  ( $\tilde{\nu} = 3550, 2800 \text{ cm}^{-1}$ ) are correlated with the water concentration determined by NRA in units of  $\text{mol} \cdot \text{l}^{-1}$  in figure 4. The data of this diagram were fitted by the equation:  $\alpha_{\text{meas}} = \epsilon_{\text{pract}} \cdot c$  in which  $\epsilon_{\text{pract}}$  is the slope of the line. The practical extinction coefficients for

Table 3. NRA and IR results for determination of practical IR extinction coefficients

glass no.	NRA $c(\text{H})$ in atom ppm	NRA $c(\text{H}_2\text{O})$ in $\text{mol} \cdot \text{l}^{-1}$	IR $\alpha_{\text{meas}}^{(2)}$ ( $\tilde{\nu}_{3550}$ ) in $\text{cm}^{-1}$	IR $\alpha_{\text{meas}}^{(2)}$ ( $\tilde{\nu}_{2800}$ ) in $\text{cm}^{-1}$	
SLS glasses	1	190	0.012	0.34	0.62
	2	310	0.019	0.57	0.95
	3	440	0.027	0.85	1.46
	4	1300	0.078	3.09	4.93
	5	2720	0.164	6.12	8.88
PLS glasses	6	130	0.0072	0.11	0.48
	7	180	0.010	0.20	0.79
	8	640	0.036	0.62	2.31
	9	2680	0.149	3.40	11.66

<sup>2)</sup>  $\alpha_{\text{meas}}(\tilde{\nu}_{3550})$ ,  $\alpha_{\text{meas}}(\tilde{\nu}_{2800})$ : maximum absorption coefficient of the IR band at about 3550  $\text{cm}^{-1}$  (2800  $\text{cm}^{-1}$ ) after subtraction of the spectrum of a theoretical "water-free" glass.

the IR bands at 3550 and 2800  $\text{cm}^{-1}$  for SLS glasses determined by combination of IR and NRA measure-

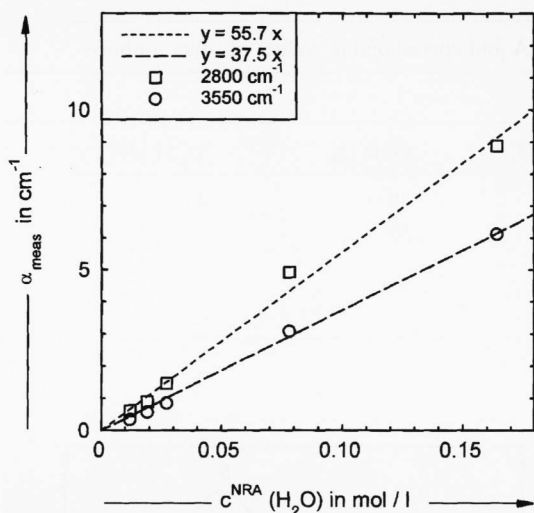


Figure 4. Maximum absorption coefficients,  $\alpha_{\text{meas}}$ , of the IR bands at 3550 and 2800  $\text{cm}^{-1}$  in the spectra of SLS glasses versus water concentration in mol/l determined by NRA and determination of the practical extinction coefficients from the rise of the straight lines fitted to the measured points.

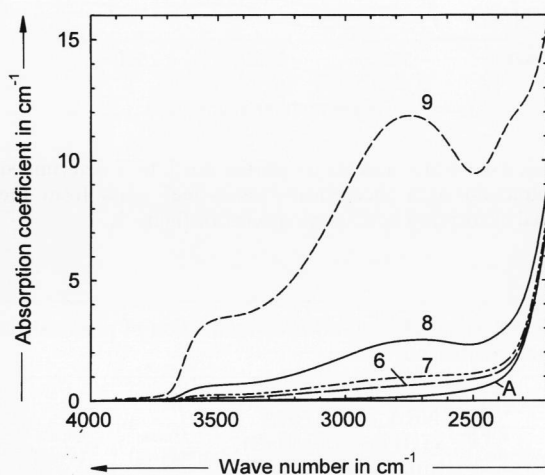


Figure 5. Absorption coefficient spectra of glasses no. 6 to 9 and spectrum of a theoretical "water-free" glass A.

ments are in a good agreement with the practical extinction coefficients determined by Götz [3] and Scholze [8] (table 2).

With the results obtained for the PLS glasses, it should be possible to determine their practical extinction coefficients. The measured absorption coefficient spectra are given in figure 5. The spectrum of the theoretical "water-free" glass is subtracted again. The difference spectra are to be seen in figure 6. Table 3 also contains the maximum IR absorption coefficients and NRA results of PLS glasses. The diagram in figure 7 shows the maximum IR absorption coefficients in relation to the

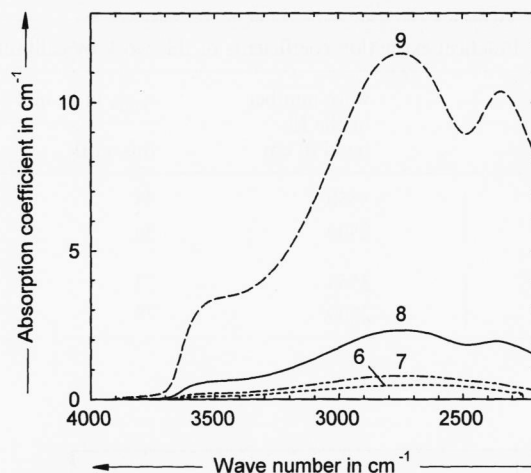


Figure 6. Pure water spectra of glasses no. 6 to 9 determined by subtraction of a theoretical "water-free" glass from the measured absorption coefficient spectra of figure 5.

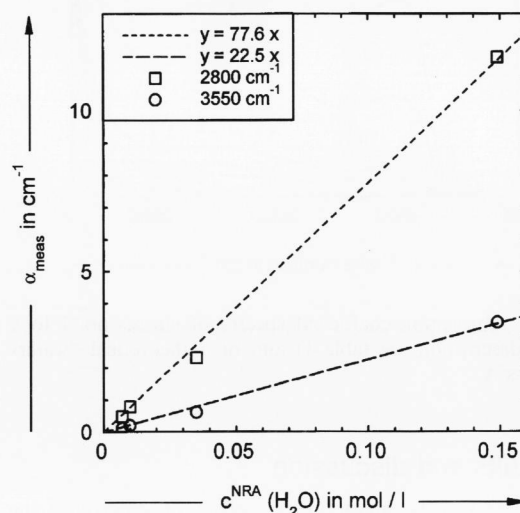


Figure 7. Maximum absorption coefficients,  $\alpha_{\text{meas}}$ , of the IR bands at 3550 and 2800  $\text{cm}^{-1}$  in the spectra of PLS glasses versus water concentration in mol/l determined by NRA and determination of the practical extinction coefficients from the rise of the straight lines fitted to the measured points.

NRA results. The data of this diagram were fitted to the equation  $\alpha_{\text{meas}} = \epsilon_{\text{pract}} \cdot c$  again. The calculated values of  $\epsilon_{\text{pract}}$  are to be seen in table 2.

In a next step, the two-band method by Scholze is applied to the IR results to determine the water content of the glass samples. For this purpose, a band separation procedure was applied to all spectra of figures 3 and 6 to calculate the band profiles without mutual overlapping. The band separation computer program "curve fit" from the "OPUS" software (Bruker) was used. As shown in figure 8, the band profiles of the three bands are not symmetrical in all cases. Asymmetrical bands were approximated by a sum of two or three symmetrical bands. The maximum absorption coefficients  $\alpha_{\text{calc}}$  ( $\tilde{\nu} = 3550, 2800 \text{ cm}^{-1}$ ), the NRA results, and the water con-

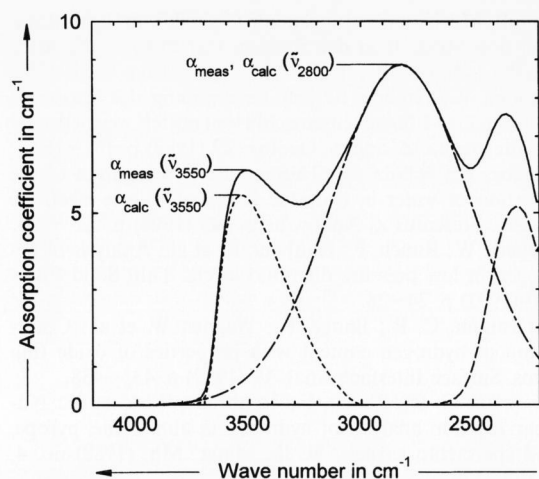


Figure 8. IR absorption coefficient spectrum of glass no. 5 (water-enriched) separated into three bands and introduction of  $\alpha_{\text{meas}}$  and  $\alpha_{\text{calc}}$ .

Table 4. Comparison of water contents deduced from IR measurements using the two-band method by Scholze and from NRA

	glass no.	IR $\alpha_{\text{calc}}^3$ ( $\tilde{\nu}_{3550}$ ) in $\text{cm}^{-1}$	IR $\alpha_{\text{calc}}^3$ ( $\tilde{\nu}_{2800}$ ) in $\text{cm}^{-1}$	IR $c(\text{H}_2\text{O})^4$ in $\text{mol} \cdot \text{l}^{-1}$	NRA $c(\text{H}_2\text{O})$ in $\text{mol} \cdot \text{l}^{-1}$
SLS glasses	1	0.31	0.62	0.010	0.012
	2	0.56	0.95	0.016	0.019
	3	0.71	1.45	0.023	0.027
	4	2.66	4.91	0.082	0.078
	5	5.47	8.85	0.157	0.164
PLS glasses	6	0.07	0.49	0.0054	0.0072
	7	0.14	0.80	0.0090	0.010
	8	0.44	2.32	0.027	0.036
	9	2.72	11.68	0.142	0.149

<sup>3)</sup>  $\alpha_{\text{calc}}(\tilde{\nu}_{3550})$ ,  $\alpha_{\text{calc}}(\tilde{\nu}_{2800})$ : maximum absorption coefficient of the IR band at about  $3550 \text{ cm}^{-1}$  ( $2800 \text{ cm}^{-1}$ ) after band separation, spectrum of the theoretical "water-free" glass subtracted before.

<sup>4)</sup>  $c(\text{H}_2\text{O})$ : water concentration within the glass calculated using the two-band method by Scholze [8], calculated according to formula (3).

concentrations obtained by IR using the two-band method are summarized in table 4. The results of the two-band method are plotted versus the water concentration obtained by NRA in figure 9. All measured points in this diagram are arranged near or on a line corresponding to the equation  $c^{\text{IR}}(\text{H}_2\text{O}) = 0.958 c^{\text{NRA}}(\text{H}_2\text{O})$ . That means, the results of the two-band method using the extinction coefficients given by Scholze agree quite well with the NRA results as well for SLS as for PLS glasses. In the PLS glasses, the fraction of "free" (very weakly

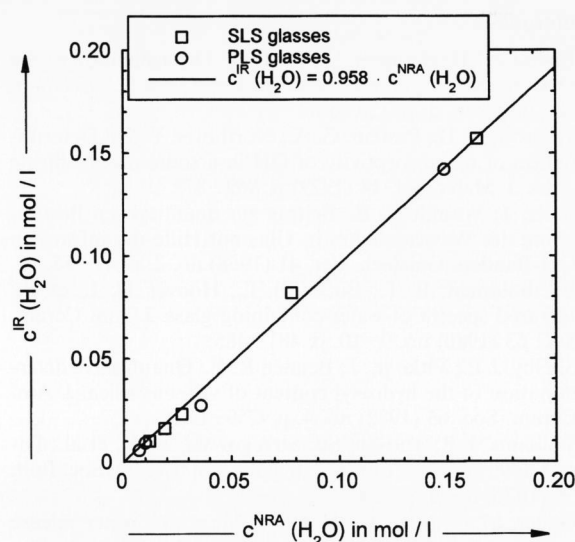


Figure 9. Water concentration of SLS and PLS glasses determined using IR spectroscopy and the two-band method by Scholze versus water concentration of the glasses by NRA measurements.

associated) OH groups is found to be much lower than in the SLS glasses, in accordance with the observations by Scholze [23] on binary alkali silica glasses.

The authors' investigations show that NRA is very well-suited for the determination of the total water content in glasses and thus, also for the calibration of the IR spectroscopy results. The practical extinction coefficients found in this way are well applicable to the determination of the water content of glasses of the same qualitative composition. But table 2 also shows the limits of the applicability of practical extinction coefficients: they must be determined for each type of glass again. However, as the results of this work on glasses with different network modifier cations (sodium and potassium) show, the two-band method by Scholze [8] seems to be suited for the determination of water in glasses of different composition.

The results obtained up to now lead to the conclusion that the method of determination of water contents of glasses from their IR spectra developed by Scholze already in the fifties is the best method still today. In future, the applicability of the two-band method to other types of glasses, especially to such of practical interest (see e.g. [24]) will have to be examined by determination of the total water content with nuclear reaction analysis.

\*

The authors thank Mrs. A. Kohl and Mrs. R. Lorenz, BAM, Berlin (Germany), for carrying out the experimental work. Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

## 5. References

- [1] Ebendorff-Heidepriem, H.; Ehrhart, D.: Determination of the OH content of glasses. *Glastech. Ber. Glass Sci. Technol.* **68** (1995) no. 5, p. 139–146.
- [2] Pearson, A. D.; Pasteur, G. A.; Northover, W. R.: Determination of the absorptivity of OH in a sodium borosilicate glass. *J. Mater. Sci.* **14** (1979) p. 869–872.
- [3] Götz, J.; Vosáňlová, E.: Beitrag zur quantitativen Bestimmung des Wassergehaltes in Glas mit Hilfe der infraroten OH-Banden. *Glastech. Ber.* **41** (1968) no. 2, p. 47–55.
- [4] Bartholomew, R. F.; Butler, B. L.; Hoover, H. L. et al.: Infrared spectra of water-containing glass. *J. Am. Ceram. Soc.* **63** (1980) no. 9–10, p. 481–485.
- [5] Shelby, J. E.; Vitko jr., J.; Benner, R. E.: Quantitative determination of the hydroxyl content of vitreous silica. *J. Am. Ceram. Soc.* **65** (1982) no. 4, p. C59–C60.
- [6] Williams, J. P.; Yao-Sin Su; Strzegowski, W. R. et al.: Direct determination of water in glass. *Am. Ceram. Soc. Bull.* **55** (1976) no. 5, p. 524–527.
- [7] Gaber, M.; Harder, U.; Hähnert, M. et al.: Water release behaviour of soda–lime–silica glass melts. *Glastech. Ber. Glass Sci. Technol.* **68** (1995) no. 11, p. 339–345.
- [8] 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. *Glastech. Ber.* **32** (1959) no. 3, p. 81–88.
- [9] Russell, L. E.: Solubility of water in molten glass. *J. Soc. Glass Technol.* **41** (1957) p. 304T–317T.
- [10] Newman, S.; Stolper, E. M.; Epstein, S.: Measurement of water in rhyolitic glasses: Calibration of an infrared spectroscopic technique. *Am. Mineral.* **71** (1986) p. 1527–1541.
- [11] Meyer, F.; Spalhoff, W.: Ermittlung des Wassergehaltes in Gläsern mit Hilfe der magnetischen Kernresonanz und Vergleich der Ergebnisse mit Messungen der infraroten OH-Banden. *Glastech. Ber.* **34** (1961) no. 3, p. 184–191.
- [12] Bartholomew, R. F.; Schreurs, J. W. H.: Wide-line NMR study of protons in hydrosilicate glasses of different water content. *J. Non-Cryst. Solids* **38 & 39** (1980) p. 679–684.
- [13] Krauß, M.: Untersuchungen zur Glasbildung, Kristallisation und Struktur in den Systemen  $\text{Sr}(\text{PO}_3)_2\text{-CaF}_2\text{-AlF}_3$ ,  $\text{Ba}(\text{PO}_3)_2\text{-CaF}_2\text{-AlF}_3$ ,  $\text{CaF}_2\text{-AlF}_3$ . Univ. Jena, thesis 1985.
- [14] Klemm, W.; Grande, S.: Zur Bestimmung des Wassergehaltes in Gas-Flüssigkeitseinschlüssen mittels magnetischer Kernresonanz. *Z. angew. Geol.* **29** (1983) p. 181–183.
- [15] Herzog, K.; Scholz, K.; Thomas, B.: Investigation of the insertion of water in hydrated layers of silicate electrode glasses. *Fresenius Z. Anal. Chem.* **349** (1994) p. 223–224.
- [16] Wagner, W.; Rauch, F.; Haubner, R. et al.: Analysis of hydrogen in low pressure diamond layers. *Thin Solid Films* **207** (1992) p. 24–28.
- [17] Ottermann, C. R.; Bange, K.; Wagner, W. et al.: Correlation of hydrogen content with properties of oxide thin films. *Surface Interface Anal.* **19** (1992) p. 435–438.
- [18] Rossman, G. R.; Rauch, F.; Tombrello, T. A. et al.: Nuclear reaction analysis of hydrogen in almandine, pyrope, and spessartite garnets. *N. Jb. Miner. Mh.* (1988) no. 4, p. 172–178.
- [19] Hammer, V. M. F.; Beran, A.; Endisch, D. et al.: OH concentrations in natural titanites determined by FTIR spectroscopy and nuclear reaction analysis. *Eur. J. Mineral.* **8** (1996) p. 281–288.
- [20] March, P.; Rauch, F.: Leaching studies of soda–lime–silica glass using deuterium- and  $^{18}\text{O}$ -enriched solutions. *Glastech. Ber.* **63** (1990) no. 6, p. 154–162.
- [21] Helmich, M.; Rauch, F.: On the mechanism of diffusion of water in silica glass. *Glastech. Ber.* **66** (1993) no. 8, p. 195–200.
- [22] Acocella, J.; Tomozawa, M.; Watson, E. B.: The nature of dissolved water in sodium silicate glasses and its effect on various properties. *J. Non-Cryst. Solids* **65** (1984) p. 355–372.
- [23] Scholze, H.: Der Einbau des Wassers in Gläsern. II. UR-Messungen an Silikatgläsern mit systematisch variiertem Zusammensetzung und Deutung der OH-Banden in Silikatgläsern. *Glastech. Ber.* **32** (1959) no. 4, p. 142–152.
- [24] 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.

■ 0198P003

## Addresses of the authors:

U. Harder, H. Geißler, M. Gaber, M. Hähnert  
Bundesanstalt für Materialforschung und -prüfung  
D-12200 Berlin

O. Dersch, F. Rauch  
Institut für Kernphysik, Universität Frankfurt  
August-Euler-Straße 6, D-60486 Frankfurt/M.