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Some aspects concerning the influence of sampling procedure on the results of gas extraction experiments [1]

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Abstract

The gas content of glass is an important factor which determines the glass quality concerning the number of bubbles and the fining behaviour. The determination of the amount of gas in glass, melted in industrial tanks is both an analytical and a sampling problem. Some difficulties are discussed concerning the determination of gas content in glass, melted in a tank, by means of modified equipment for evolved gas analysis. It could be shown that the variance of the gas content in a blob is strongly influenced by sampling procedure and not only by gas distribution in the melt.

INTRODUCTION

The term "gas content" is commonly used to discuss the fining behaviour of a glass melt or is restricted only to the definition of volatile compounds detected in bubbles or blisters under normal temperature conditions. Only a few publications are known with quantitative data concerning the relation between the volatile concentration in the glass melt and the quality of the final product [1, 2].

It seems that two aspects are of primary importance for further investigation in the field of gas extraction experiments. Firstly, the exact semantic definition of the terms "volatile" and "gas content of glass", for example, the characterization of the oxygen content of silicate glass [3]. Secondly, the discussion of the term "gas content" considering the influence of various parameters arising during sample preparation (e.g. sampling methods, sampling intervals).

The aim of the present paper is to show that a specialized method of evolved gas analysis (EGA) can be used for characterizing the gas content

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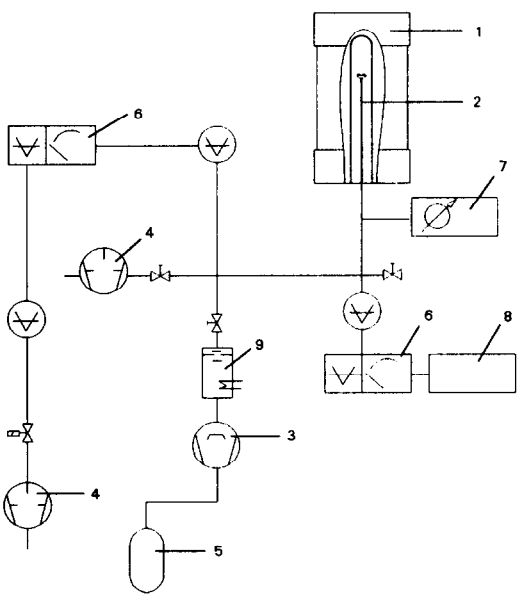
[1] Dedicated to Hans Georg Wiedemann.

of technical glass including the influence of the above mentioned parameters.

EXPERIMENTAL

In 1960, Hans Wiedemann introduced a thermobalance which was the "nucleus" of a very successful development in the field of thermal analysis [6]. The equipment referred to in this paper was developed from the Hans Wiedemann TA1-conception in order to solve special problems in glass research.

The experimental set-up used is shown in Fig. 1 and described in detail in ref. 4. The following experimental conditions are realized: sample size, ground glass, grain size (0.4–0.63 mm); sample mass, 30.0 mg; crucible, Al_2O_3, cylindrical, burned out in the Bunsen burner; atmosphere, vacuum ($<2 \times 10^{-5}$ Pa); heating rate, 25 K min^{-1} from 20°C to 850°C and 10 K min^{-1} from 850°C to 1400°C; temperature measurement, at the bottom of the crucible (calibrated reference material).



1- furnace
2- sample holder
3- oil diffusion pump
4- rotary pump
5- storage jar
6- vacuum gauge
7- temperature gauge
8- y-t recorder
9- cold trap

Fig. 1. Schematic diagram of the experimental set up.

DEFINITIONS

The characteristics and parameters used for the definition of the degassing behaviour are according to Fig. 2. The number of peaks (BZ) is the number of spontaneous total pressure changes in the temperature–pressure diagram in a selected temperature range. The sum of intensity of

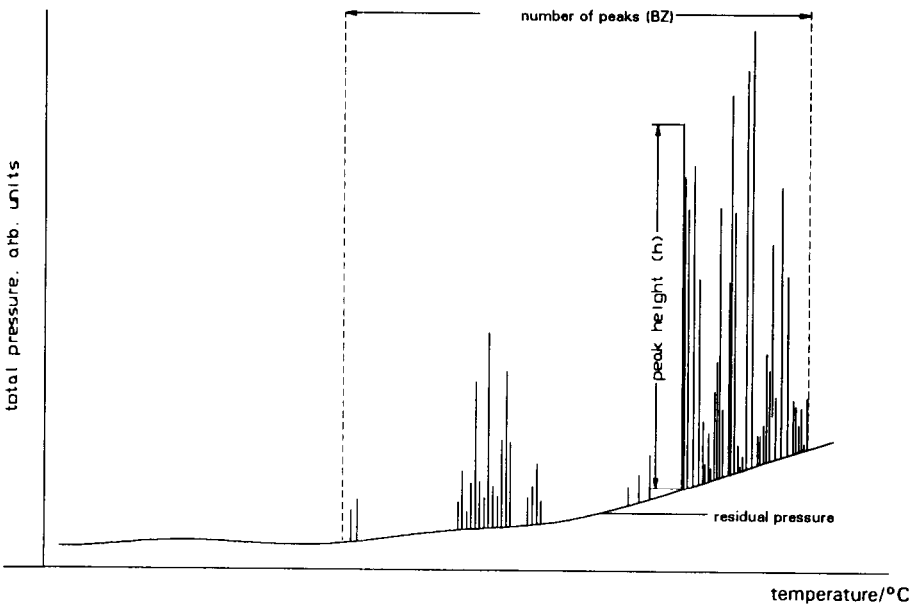


Fig. 2. Graphical representation of the number of peaks (BZ), the sum of intensity of the spontaneous pressure changes $\sum I$ (equals the gas content), the height of the peak (h).

the spontaneous pressure changes ($\sum I$) (equals the gas content) is the sum of pressure differences between the residual pressure in the recipient before and after the bursting of a bubble (sudden peak occurs). The sum of intensity is a relative value for the extractable gas volume per sample. The height of the peak (h) in arbitrary units is the pressure difference between the initial pressure (residual pressure in the recipient) and the highest point of the peak.

The ratio ($\sum I$/BZ) corresponds to the volume of evolved gas per bubble (in arbitrary units).

The degassing behaviour of the glass determines the correlation between temperature and total pressure under high vacuum conditions.

RESULTS

The EGA method mentioned above permits the determination of the gas content of optical and TV-glass [5] with a standard deviation of approximately 5%. In contrast to these results the gas content of conventional container glass was determined with a standard deviation of about 30%.

It seems that in addition ot the known factors which influence the gas content, e.g. quality of the raw material, throughput, concentration and type of fining agent, cullet ratio, etc., the following conditions also play an

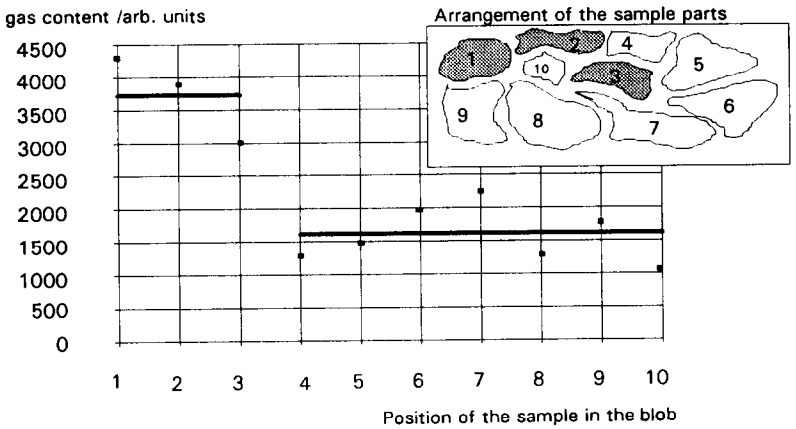


Fig. 3. Variation of the gas content depending on the sampling position in the blob.

important role: (1) locality of sampling, discussed in ref. 4; (2) inhomogeneities in the distribution of volatile in the micro range (Fig. 3); (3) sampling time, interval of sampling (Fig. 4).

The distribution of gas content in the bulk of a blob is illustrated in Fig. 3. Two fields of different gas content can be distinguished. Field I (grey), consisting of samples 1, 2 and 3, characterizes the zone of "high" gas content. The zone of "low" gas content, field II (white), comprises the samples 4, 5, 6, 7, 8, 9 and 10.

Figure 4 demonstrates the changes observed in the gas content of a colourless container glass in relation to the sampling time. Oscillation of the gas content is an obvious characteristic in this case. Also after repetition of the measuring series (1) by another operator, the curve (2) shows a nearly identical course.

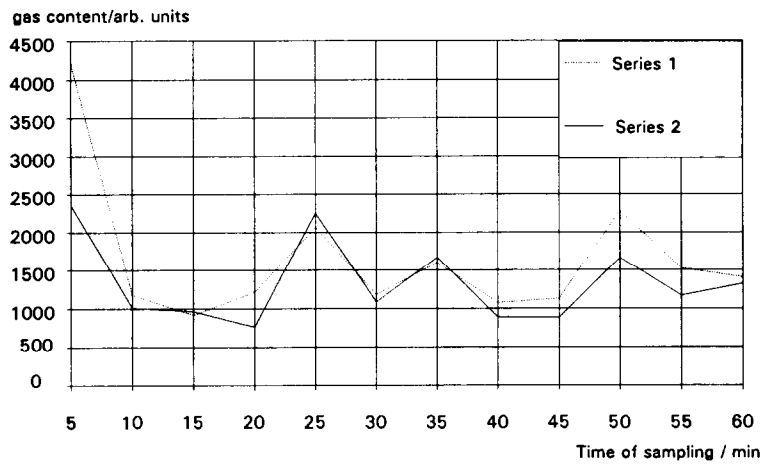


Fig. 4. Variation of the gas content depending on the time of sampling.

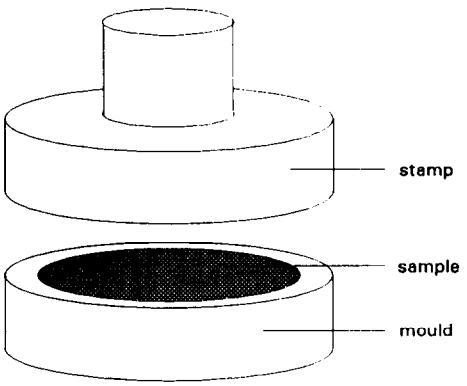


Fig. 5. Sampling device.

The sampling procedure was modified to minimize the influence of sampling time and sampling position on the results. The sample was taken from directly between the feeder and the glass forming machine by the special sampling device which is shown in Fig. 5. After removing the sample, the stamp was immediately pressed onto the surface of the mould. The advantages of this new sampling method are, (i) sampling of a constant sample mass (about 30 g) independent of the mass of the blob, (ii) defined sample cooling conditions (all surfaces of the sample contact the metal walls of the sampling device), (iii) the sample can be used for X-ray analysis.

Table 1 shows an example of the results of gas extraction experiments on

TABLE 1

Degassing behaviour of amber glass (container glass) samples A and B [a]

Sample/Run	T_{EB}/°C	BZ	$\sum I$/arb. units	Standard deviation σ/% of $\sum I$, BZ and T_{EB}
A/1	975	148	1468	
A/2	940	159	1565	$\sum I$ 4
A/3	970	160	1482	BZ 7
A/4	965	171	1530	T_{EB} 2
A/5	985	177	1610	
B/1	980	164	1364	
B/2	980	165	1458	$\sum I$ 3
B/3	960	151	1425	BZ 4
B/4	960	163	1467	T_{EB} 1
B/5	960	167	1449	

[a] Place of sampling, glass factory Freital, Germany, melting tank B, feeder 1; time between sampling A and B, 24 h; maximum extraction temperature, 1450°C; number of measurements, 5.

two amber glass samples (A and B) using the described sampling procedure.

DISCUSSION

The modified EGA method, as described, permits the determination of degassing characteristics of glass, melted in large scale tanks and sampled from these tanks.

The "gas content" of standard container glass oscillates, considerably exceeding the standard deviation caused by this method. The highly heterogeneous distribution of the dissolved gases is one reason for the high standard deviation and makes the interpretation of results extremely complicated. So far no reliable explanation can be given for this inhomogeneous gas distribution in the melt.

The gas content is also influenced by sampling time with both short and long intervals between sampling. This behaviour as a function of time should be discussed in combination with the glass flow conditions in the tank.

The exact separation of factors influencing the detectable gas content is absolutely necessary for the preparation and evaluation of gas extraction experiments. The influence of sampling position and sampling time on the degassing behaviour of the samples can be reduced to the standard deviation caused by the experimental procedure (approx. 5%) using a well defined sampling method.

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