Original Paper

Density titration – A simple method for the determination of density variations in glasses

Wolfgang Muschick
Schott Glaswerke, Mainz (FRG)

By modifying the well-known sink-float method it is possible to determine density differences in solid glasses either with a very simple procedure or in a very exact way. The density of the immersion fluid is altered in the proposed way by adding another fluid to it at constant temperature in controlled steps. It was found that tetrabromethane (TBE) and methanol is a suitable pair of fluids for this kind of measurements.

A simple apparatus, the procedure and some illustrating examples of the successful use of the proposed way are described.

Dichtetitration – Ein einfaches Verfahren zur Messung von Dichteunterschieden in Gläsern

Durch Modifizierung der bekannten Schwebemethode wird es möglich, Dichtedifferenzen in Gläsern entweder mit einem einfachen Verfahren oder auch mit hoher Genauigkeit zu ermitteln. Bei dem vorgeschlagenen Weg wird die Dichte der Immersionsflüssigkeit durch Zutitrieren einer anderen Flüssigkeit bei konstanter Temperatur verändert. Ein hierfür geeignetes Flüssigkeitspaar ist Tetrabromäthan (TBE) und Methanol.

Es werden eine einfache Meßvorrichtung, die Vorgehensweise und einige die erfolgreiche Anwendung illustrierende Meßbeispiele beschrieben.

1. Introduction

The knowledge of the amount of density differences in glass samples can help in two different ways. If there are apparent inhomogeneities in a product, the knowledge of the density differences between inhomogeneities and homogeneous glass can help in finding the source of the fault. In glass pieces without apparent faults, the degree of the density spread can give some idea of the general level of chemical homogeneity.

The most common method of measuring density differences in glass is to observe the movements of the sample in an immersion liquid whose density is changing. Normally, the density of the liquid is changed by altering the temperature. This can be done by time-dependent changes [1 and 2] (sometimes with the aid of a centrifuge [3 and 4]) or by building up a controlled temperature gradient [5]. With both methods, the precision depends on the reproducible adjustment of small temperature differences, which is much more difficult than keeping the temperature constant. The density of the immersion liquid can also be altered by high pressure [6]. But, by this way, only relatively small density changes are possible. In this contribution, a simple procedure for determining density differences in glasses is shown, whose precision depends only on the degree of temperature stability.

Presented in German on 27 May 1986 at the 60th Annual Meeting of the German Society of Glass Technology (DGG) in Bremen.
Received 26 September 1986.

2. Description of the method

In the proposed way of determining density differences in glass, the density of the immersion liquid is altered by mixing it with another fluid of different density. This mixing is accomplished in a controlled manner and at constant temperature. Precondition is that the two liquids behave similarly to an "ideal" mixture. The density should be more or less linearly dependent on the composition. Figure 1 shows that the liquid pair tetrabromethane (TBE) and methanol fulfills this requirement in the interesting concentration range quite well. Methanol can easily be removed from the mixture again by a slight vacuum treatment.

Figure 2 shows an example of a simple measuring apparatus. The sample and a definite volume of TBE is filled into a measuring cylinder with a magnetic stirrer at the bottom. To keep the temperature constant, the measuring cylinder is standing in a glass Dewar vessel filled with a water–ice mixture. After approaching thermal equilibrium, methanol is added in controlled steps. After every addition, the immersion mixture is thoroughly mixed by the magnetic stirrer.

From the amount of methanol which has to be added till the glass sample is beginning to sink, the

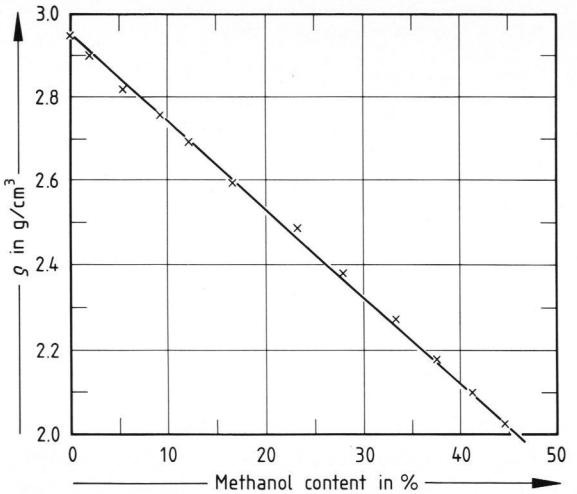

Figure 1. Density of immersion mixture as a function of the methanol content.

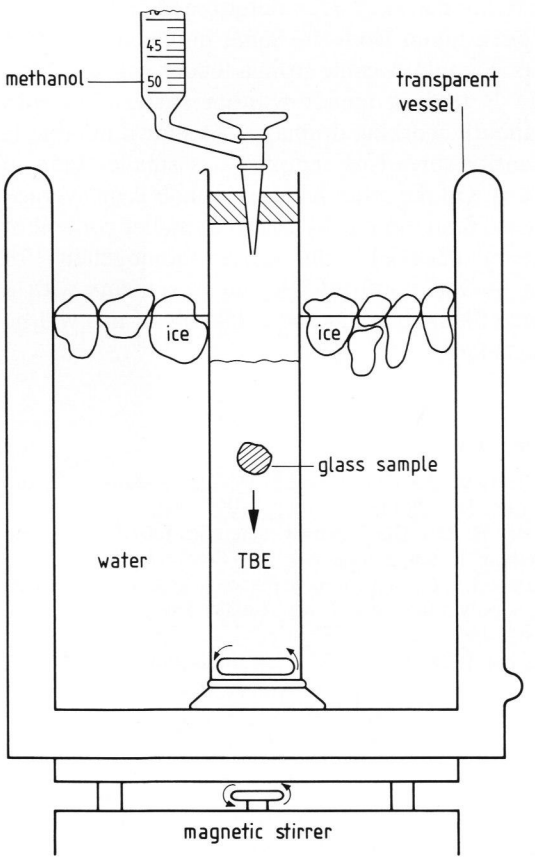

Figure 2. Example for a simple measuring apparatus.

density of the sample can be evaluated. With several glass pieces or powders, the amount of methanol between the first and the last piece or particle sinking gives information about the density spread. At the determination of the density spread in glass powders, a problem arises in choosing the best grain size. On the one hand, the grain size must be so small that density differences between different samples can be seen clearly enough. On the other hand, the density

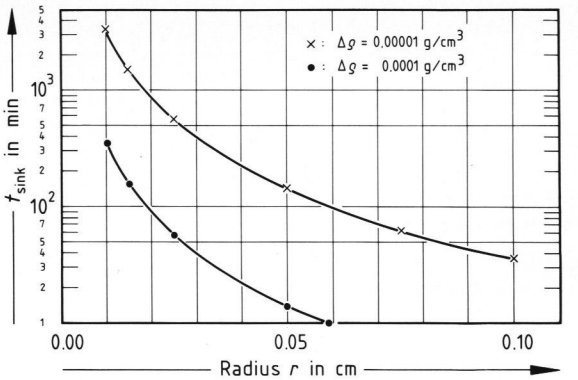

Figure 3. Time for sinking 1 cm as a function of grain size and density differences in the immersion mixture. (Assumption: spherical particles.)

determination is becoming more time-consuming with smaller grain size. As can be seen in figure 3, the movement of small grains is becoming very slow at small density differences to the immersion mixture (high levels of resolution).

Several samples from different borosilicate tanks were examined. It was found that the differences in the density spreads between the samples were qualitively the same up to the grain size in the region of 1 to 0.9 mm.

3. Precision of the method

The main advantage of the proposed method is its simplicity. But basically, by this way, also high precision can be achieved. This is because the density steps of the immersion mixture can be made as small as necessary by premixing the liquid pair. The limits of the precision are given by the degree of temperature stability. In the temperature region between 0 and 10 °C, the temperature dependence of the density of the liquids allows a precision of 10^{-5}, for instance, at a temperature stability of 0.01 K. The same degree of precision without any temperature problems can be achieved by measuring the density of the liquid pair on-line with a commercially available apparatus (producer: A. Paar KG, Graz (Austria)). In this case, one has only to take care that there are no temperature differences between the measuring cylinder and the apparatus.

In reality, the limits of precision, especially with small glass pieces, are determined by the patience of the operative. With small density differences, the movement of the samples is becoming very slow. The actual density values gained from the experiments tended to be too small. One reason for this may be that a thin film of air or tiny air bubbles on the surface of the samples falsify the result. This can be supposed on grounds of the experimental finding that the deviations are growing with decreasing size of the glass pieces. Further investigations in this direction have to be made.

Table 1. Density spread (in ml methanol) of glass samples from different feeders of a borosilicate glass tank

	addition of methanol to TBE in ml		differences of methanol addition in ml	mean value of methanol addition in ml
	first particle sinking	last particle at bottom		
sample A (feeder with stirrer)	24.72	25.53	0.81	25.13
sample B (feeder with drainage)	24.89	26.12	1.23	25.51

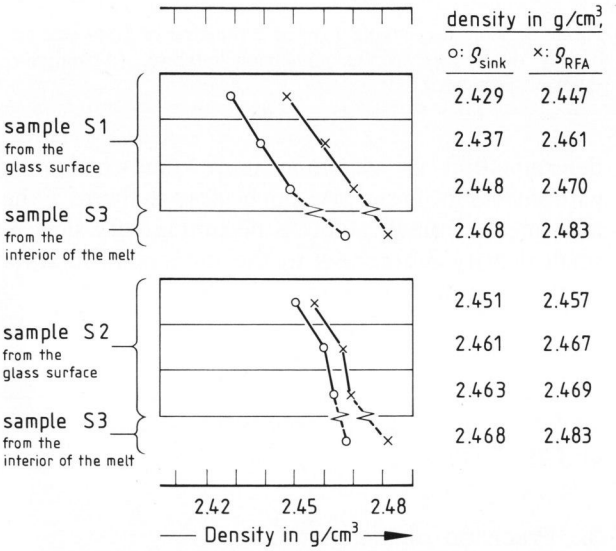

Figure 4. Density gradients in glass samples from the surface of a fining tank. ○ = determined by the modified sink-float method; × = evaluated from the composition.

4. Practical examples

Two examples shall serve as an illustration of the possibilities of the proposed method.

In the first example, density differences between relatively large glass pieces (≈ 1 g) have been determined and compared with data derived from the composition. Two samples (S 1 and S 2) from the mirror of a refining tank had been cut into 3 sections with a different distance to the melt surface (figure 4). By using the proposed method, the density of these sections has been determined and compared with that of a glass sample (S 3) more from the interior of the melt. By RFA measurement in layers, the chemical composition of the interesting region has been determined. With the increments of Huggins and Sun [7 and 8], and the mean chemical composition, the mean densities of the 3 sections have been evaluated. In figure 4 can be seen that the absolute values determined by the proposed method are lower than the calculated densities. The various density gradients in the two samples (due to the volatilization of alkali oxide) are comparable for both methods.

In the second example (samples A and B), the density spread in two different glass powders (grain size 1 to 0.9 mm) has been determined. The samples have been taken from the same tank, but different feeders. Sample A came from a feeder with a stirrer, sample B from a feeder without stirrer, but with permanently working drainage. As shown in table 1, the density spread of sample A is smaller than in sample B. On the other hand, sample B is on average less dense than sample A, due to a smaller content of refractory material. The better homogeneity of sample A was confirmed by measurements with a modified Shelyubskij method. Details of this will be reported later.

5. References

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