

## DETERMINATION OF GAS PROPERTIES IN GLASS MELTS

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*The paper summarizes experimental methods of measurement of gas properties needed for the description of the interactions gas - glass melt. The combination of the melt extraction, gas chromatography, electrochemical methods and visual observation of bubble behaviour or absorption of the defined volume of gas in the melt is used for the determination of diffusion coefficients, actual concentrations and solubilities in the melts. In addition, the gas chromatography and mass spectrometry are used for the analysis of gases evolved during heating of glass batch making possible to study important reactions in early stadium of the melting process. Equilibrium constants of redox reactions are measured by indirect method when combining electrochemical measurement of oxygen equilibrium partial pressure and chemical analysis of redox species in quenched samples. The gas properties in glassmelts may be simultaneously obtained by the observation of growth or dissolution of defined bubbles and by their subsequent analysis. The evaluation procedure comes from equations of bubble behavior. One gas property, either physical solubility or actual concentration in the melt should be however ensured by above described method. To examine only the rate of the refining process, the values of the bubble growth rates are measured and subsequently used in the simplified mathematical model.*

### INTRODUCTION

The interactions between gases and glass melts are important part of melting process. The most frequent gases being present both in glass-melt and bubbles and transferred between them are water vapor, oxygen, sulfur dioxide, carbon dioxide, nitrogen and argon. These gases play thus the main role in the glass fining process and bubble defect behavior in glasses.

Mentioned processes may be successfully studied by mathematical modeling [1-11]. The simulation is usually based on the elementary model of single bubble behavior describing the growth, dissolution and composition changes of a multicomponent bubble. The modeling of bubbles results in description of bubble rising velocities, their pathways in the melting space starting from bubble sources, their concentration fields in the space [12] and bubble influence on the melt properties and behavior [13]. The composition of bubbles leaving the melting facility confronted with defect bubble analyses gives information about nature and location of a bubble source inside of the melting space.

The accuracy of bubble modeling is dependent from the experimental data needed by bubble equations.

The data of present gases play here a crucial role. In order to be able simulate bubble behavior, the temperature-dependent diffusion coefficient, solubility and actual bulk concentration of each gas transferred between a bubble and melt should be known. In addition, chemically dissolved gases need information about their equilibrium concentration in the melt, the value of the equilibrium constant is therefore measured. The aim of the paper is to summarize experimental methods of measurement of gas properties needed for the mathematical simulations of the interactions gas-glass melt.

### DIRECT DETERMINATION OF GAS PROPERTIES

The acquisition of above mentioned data represents a very troublesome experimental task. The measurements at high temperatures, low values of diffusion coefficients (usually between  $10^{-9}$  and  $10^{-12}$  m<sup>2</sup>/s), as well as extremely low gas physical solubilities and actual concentrations in glass melts (usually between  $10^{-2}$  and  $10^{-3}$  kg/m<sup>3</sup>), restrict the both chances of experimental methods and accuracy of acquired data.

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Determination of gas solubilities and actual concentrations

The usual methods of solubility and concentration measurements are composed of two steps, the first one involving liberation of dissolved gases from the melt and the second one their analysis [14]. The liberation of gases may be performed both by vacuum extraction and by flushing out the melt by an inert gas of high purity. In order to determine the liberated gases, the gas chromatographic or mass spectrometric methods are used.

Figure 1 presents the scheme of the method of helium extraction followed by gas chromatographic determination of extracted gases.

The sample is placed in the silica test tube located in the laboratory furnace (1). The gases evolved from the sample into the stream of stripping gas (helium) are trapped in the concentration tube placed in liquid nitrogen (2). After finishing the extraction, the concentration tube is heated in hot oil and connected via six-port valve (3) with gas chromatograph. Two capillary column system is used for the GC separation of the analyzed gases - Gas Pro (4) and Molecular Sieve (5). The separated gases are subsequently carried into Thermal Conductivity or Mass Spectrometric Detector (7). The method is not able to analyze the content of dissolved water, which is determined separately by infrared spectrometry [15].

When measuring the gas solubility in the melt, the melt is bubbled by the given gas at given temperature for different times prior to gas analysis. The solubility value is obtained from the maximum of the saturation curve representing the dependence of the gas content on the saturation time (Figure 2).

The method of gas chromatography may be modified for the analysis of gases evolved from glass batches. As can be seen from the Figure 3, the sample is placed in silica cell, which is placed in laboratory furnace heated usually by a heating rate of 5°C/min.

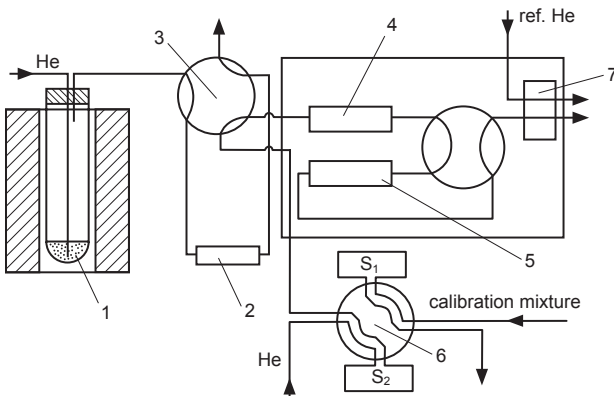


Figure 1. The determination of actual gas concentration in the glass melt.

The silica vessel is flushed by helium flowing into sampling loops having known volume. The sampling loops are repeatedly switched into the stream of carrier gas of the chromatograph. The results of analyses having the form of temperature dependence of evolved gases amount are used to study the decomposition of batch component or their mutual interactions [16]. Figure 4 presents the example of EGA analyses of glass batches containing different amounts of sulphate and carbon [17].

Determination of diffusion coefficients

The principle of the method is obvious from Figure 5 [18]. The measured gas is introduced by the Pt tube into the closed cylindrical silica glass vessel being suspended above glass level in the silica glass pot with glass. The cylindrical vessel with the measured gas is then immersed into the glass melt. The gas absorption by the glass melt is indicated by rising the glass level inside the cylindrical vessel. The rising of glass level is recorded and its time development is subsequently used

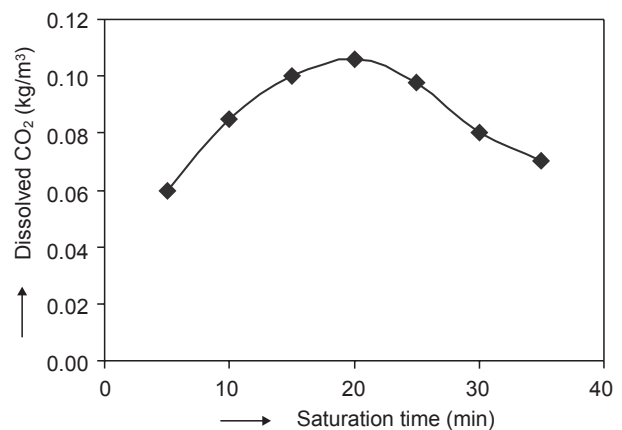


Figure 2. The CO<sub>2</sub> content vs. saturation time. TV glass, temperature 1300°C.

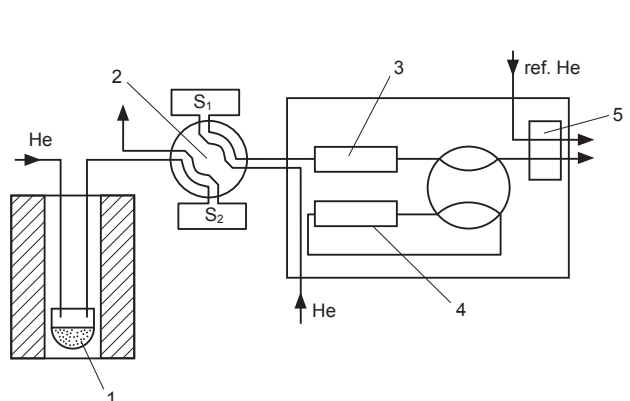


Figure 3. The scheme of the method of Evolved Gas analysis.

for the calculation of the diffusion coefficient. As the diameter of the cylindrical vessel is relatively small (less than 10 mm), the shape of glass level inside may be considered spherical, thus characterized by the curvature radius  $r_a$ . The diffusion surface  $S$  between glass and gas is given by:

$$S = 2\pi r_a^2 (1 - \sin \alpha) \quad (1)$$

where  $\alpha$  is the contact angle between glass and silica glass vessel. Using the solution of the second Fick's law in spherical coordinates [18], the following equation holds after integration for the mass balance at the phase boundary glass melt–gas:

$$h - h_0 = -\frac{DRT}{pM} \frac{2r_a^2}{r_o^2} (1 - \sin \alpha) (c_i - c_b) \left[ \frac{\tau}{r_a} + 2 \left( \frac{\tau}{\pi D} \right)^{1/2} \right] \quad (2)$$

Here  $h$  and  $h_0$  are the actual and initial height of the glass level in the vessel,  $R$  is the gas constant,  $r_o$  is the radius of the vessel,  $T$  is absolute temperature,  $p$  is pres-

sure,  $M$  is the molecular mass of the measured gas and  $c_i$  and  $c_b$  are the interfacial and bulk concentrations of the measured gas in the melt.

### Determination of equilibrium constant of polyvalent elements

Measurement of equilibrium constants of redox reactions involves determination of equilibrium concentration (partial pressure  $p_{O_2}$ ) of dissolved oxygen and the equilibrium redox ratio of given polyvalent element. Both direct and indirect methods are used in the laboratory practice. Indirect methods separate the determination of oxygen and the redox ratio in two steps. Commercially available oxygen sensors make possible to get the  $p_{O_2}$  value in the melt at the experimental temperature. The redox ratio is then obtained after quick cooling the sample by wet chemical or physical methods. Big problem of indirect methods is that only one polyvalent element has to be present in the glass. In addi-

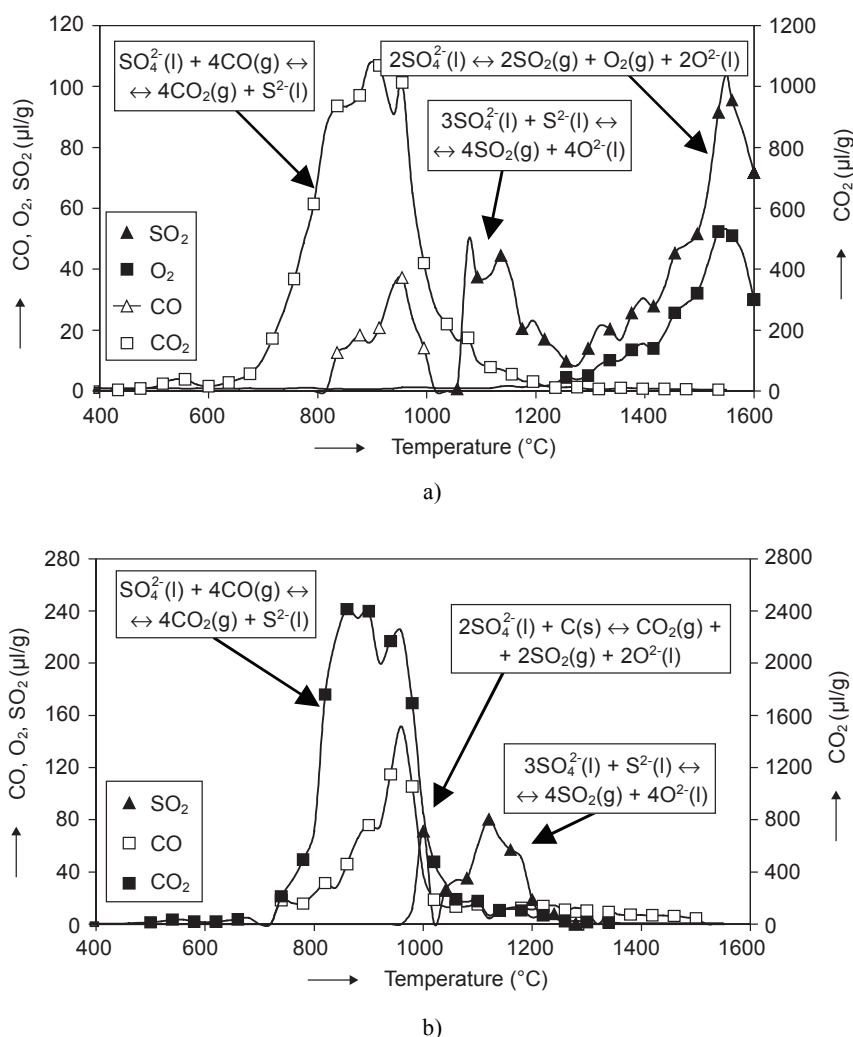


Figure 4. EGA analyses of glass batches containing sulphate and carbon. a) C/SO<sub>4</sub><sup>2-</sup> = 0.5; b) C/SO<sub>4</sub><sup>2-</sup> = 2.0

tion, the equilibrium redox ratio may be changed during sample cooling or during the sample decomposition prior to wet chemical analysis.

Direct methods determine both equilibrium  $p_{O_2}$  and redox ratio at high temperature by the electrochemical methods, most frequently by square-wave voltammetry [19].

#### Determination of sulphate equilibrium constant

The experimental arrangement of the proposed method is similar to that of the determination of diffusion coefficient (Figure 6a). The gas mixture with defined partial pressure of the stoichiometric mixture  $2SO_2 + O_2$  is introduced in the cylindrical vessel placed above the glass melt in the observation cell. The vessel is then immersed into the melt. As the initial partial pressure of the stoichiometric mixture is higher than expected equilibrium one, the gas volume inside the vessel starts to dissolve quickly in the melt to reach the equilibrium with known sulphate content dissolved in the melt (Figures 6b, c).

The determination of equilibrium partial pressure of the stoichiometric mixture is based on a simple mass balance

$$p_{eq}V_{eq} = p_iV_i - 101.3 (V_i - V_{eq}) \quad (3)$$

where  $p_i$  are partial pressures of the mixture and  $V_i$  are gas volumes calculated from geometrical dimensions of the gas volume measured by image analysis.

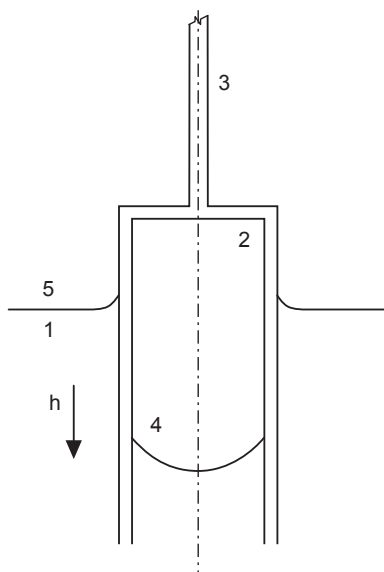


Figure 5. The scheme of the experimental arrangement. 1 - the observation silica glass cell; 2 - the cylindrical silica glass vessel with measured gas; 3 - the holder; 4 - moving interface between gas and glass melt.

#### THE GAS DATA ACQUISITION BY THE COMBINATION OF THE BUBBLE BEHAVIOUR MODEL AND EXPERIMENTAL METHODS

The application of mathematical models of gas–glass melt interactions is considerably affected by the accuracy of the experimental methods used for the obtaining demanded gas properties. Especially very low values of gas physical solubility however bring considerable errors of experimental values restraining the applicability of the models. Therefore, parallel approaches to the gas properties acquisition are developed.

#### The model modification for gas data acquisition

The set of differential equation simulating the behaviour of multicomponent bubble in the glass melt [8,9] can be at isothermal conditions arranged into the form convenient for calculation of the products invol-

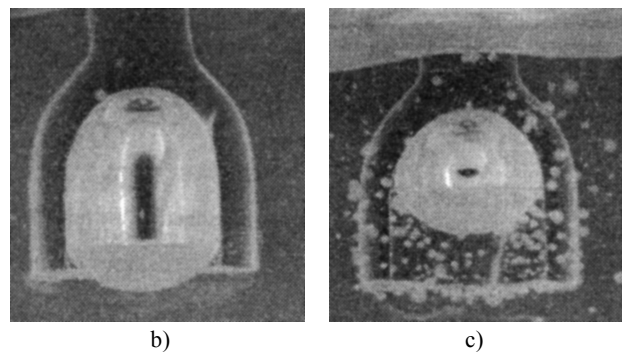
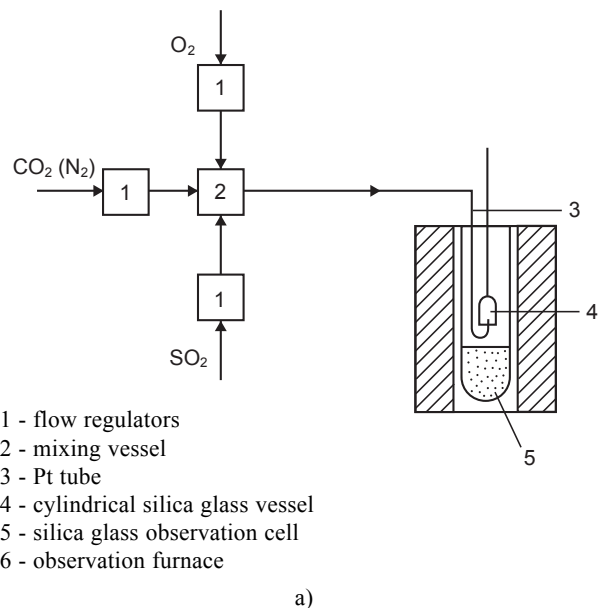


Figure 6. The determination of sulphate equilibrium constant. The scheme of the method (a). The initial and the final stage of the experiment (b, c).

ving actual concentration, solubility and diffusion coefficient of the *i*-th gas [20]:

$$D_i^{2/3} L_i = \frac{a_{j+1} M_i}{3A(p_{ij} - p_{i,j+1})} \left[ \frac{dp_{i,j+1}}{d\tau} + \frac{3p_{i,j+1}}{a_{i+1}} \frac{da_{j+1}}{d\tau} - \frac{a_j}{a_{j+1}} \frac{dp_{ij}}{d\tau} - \frac{3p_{ij}}{a_{j+1}} \frac{da_j}{d\tau} \right] \quad (4)$$

$$D_i^{2/3} m_{ib} = \frac{a_j M_i}{3A} \frac{dp_{ij}}{d\tau} + D_i^{2/3} L_i p_{ij} + \frac{M_i p_{ij}}{A} \frac{da_j}{d\tau} \quad (5)$$

where  $a_j$ ,  $a_{j+1}$  and  $p_{ij}$ ,  $p_{i,j+1}$  are the bubble sizes and partial pressures of the measured gas in the bubble in two experimental times, *j* and *j*+1,  $M_i$  is molecular weight of the *i*-th gas and  $A$  is the constant:

$$A = \frac{0.382RTg^{1/3} \rho^{1/3}}{\eta^{1/3}} \quad (6)$$

Here  $\rho$  and  $\eta$  are the glass density and viscosity and  $g$  is the acceleration of gravity. Several appropriate couples of bubble sizes and gas concentrations measured in the non-stationary region are always taken into calculations to obtain the average value of products in Equations (4-5). To get separate values of  $D_i$ ,  $m_{ib}$  and  $L_i$  from both products, one value, usually gas concentration should be determined by the experimental methods discussed in previous paragraphs. The acquisition of the  $da/d\tau$  and  $dp_i/d\tau$  values is made by the semi empirical equations fitting the experimental dependences:

$$a = (a_o - a - k_1\tau) \exp(-k_2\tau^{k_3}) + a + k_1\tau \quad (7)$$

$$p_i = (p_{oi} - p_{istat}) \exp(-k_4\tau^{k_5}) + p_{istat} \quad (8)$$

where  $a_o$  and  $p_{oi}$  are initial values of bubble size and gas partial pressure in the bubble,  $k_1$ - $k_5$  are empirical constants,  $p_{istat}$  is the stationary partial pressure of the *i*-th gas in the bubble, and  $a$  is the bubble size obtained by elongation of the linear part of bubble size development to zero time.

#### The experimental procedure of bubble observation

The method of high temperature observation of gas bubble in a glass melt is used to get the experimental dependences  $a = a(\tau)$  and  $p_i = p_i(\tau)$  mentioned in previous paragraph. The glass sample is inserted into a flat silica glass observation cell and heated to the measuring temperature in the laboratory furnace with an observation window. After glass melting and refining, a small bubble of defined initial composition is created by the silica glass tube with inlet of defined gas and immersed in glass. The bubble is subsequently "shuttled" in the glass melt by cautious and slow sucking and expelling the bubble into or out of the silica glass tube as is schematically presented in Figure 7.

The bubble size development is continually recorded by a digital camera. Figure 8 presents an example of a high temperature image. After finishing the experiment, the small glass sample with the examined bubble is taken out from the melt and cooled. The bubble composition is determined by the mass spectrometry.

#### SIMPLIFIED MODEL OF BUBBLE BEHAVIOUR

Simplified model of bubble behaviour is based on the idea, that any multicomponent bubble in the glass melt reaches, after sufficiently long time, the stationary composition, which is independent from initial composition and under given conditions depends only on concentration of gases dissolved in the melt. Under non-isothermal conditions, the time change of the stationary bubble size can be expressed by the equation [21]:

$$\frac{da}{d\tau} = \left( \frac{da}{d\tau} \right)_D + \frac{a}{300-3C} \frac{dC}{d\tau} \quad (9)$$

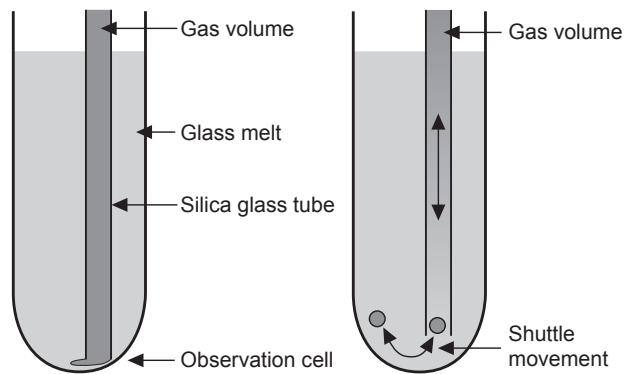


Figure 7. Scheme of the "shuttle" method.

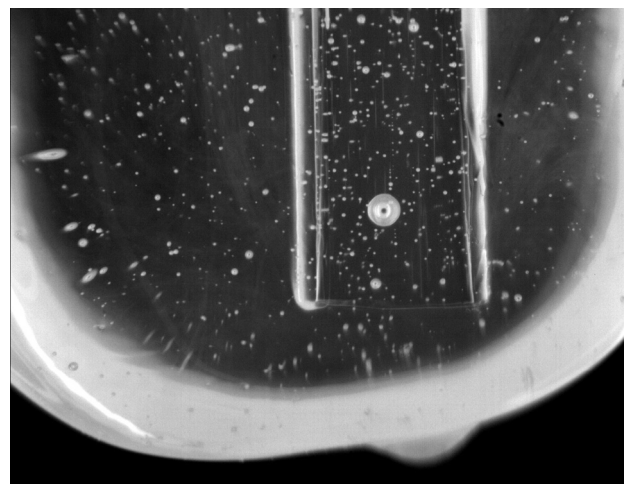


Figure 8. Micrograph of high temperature observation of a bubble in the laboratory furnace.

The first term on the right side represents linear bubble growth or dissolution at constant temperature and the second one change of the bubble size with the temperature given by the change of the content of refining gas in the bubble  $C$ . Both quantities, i.e. almost linear bubble growth or dissolution and the content of the refining gas are measured experimentally by the method mentioned in previous paragraph and by the measurement of the bubble shrinkage at sudden temperature drop.

## CONCLUSION

The application of the bubble model needs proper values of particular quantities characterizing gases, namely their diffusion coefficients, solubilities and bulk concentrations (taking into account also chemical solubility of some gases). The values are acquired by laboratory measurements using different laboratory methods as are high temperature extraction of gases from the melt and their subsequent determination by gas chromatography, different methods of gas diffusivity measurements and measurements of chemical equilibria of gases in melt. The limited accuracy of these methods however frequently restrains the quantitative applicability of the mathematical modeling.

The laboratory bubble observations seem to be sensible method which can help to obtain majority of demanded data. In addition, the laboratory observation can well serve to the verification of the models of single bubble behaviour.

## Acknowledgement

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## STANOVENÍ VLASTNOSTÍ PLYNŮ VE SKLOVINÁCH

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Práce podává přehled experimentálních metod stanovení vlastností plynů potřebných k popisu interakcí mezi plynou fází a sklovinou. Kombinace extrakce taveniny, plynové chromatografie, elektrochemických metod a vizuálního sledování chování bublin nebo absorpce definovaného objemu plynu v tavenině se využívá ke stanovení difúzních koeficientů, skutečných koncentrací a rozpustností plynů ve sklovinách. Rovnovážné konstanty redox reakcí se měří nepřímými metodami, které kombinují elektrochemické měření parciálního tlaku kyslíku ve sklovině a chemickou analýzu redox složek ve vzorku skla po ochlazení. Vlastnosti plynů ve sklovinách mohou být současně stanoveny pozorováním chování bublin a jejich následnou analýzou. Jedna z vlastností plynů, obvykle skutečná koncentrace nebo rozpustnost, však musí být stanovena některou z výše popsaných metod. Pro hodnocení účinnosti čerčicího procesu jsou měřeny pouze hodnoty rychlosti růstu bublin, které jsou následně využívány zjednodušeným matematickým modelem.