

PRODUCTION PLANNING IN GLASS MANUFACTURE BY MEANS OF THERMAL ANALYSIS

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The possibility of modified thermal analytical techniques is discussed with respect to the control and optimization of glass production.

Calorimetry and EGA-measurements are particularly interesting. A 'reversed' drop calorimeter is described for the determination of the energy expended in the heating of a glass batch into the original state of constitution.

A piece of special EGA-equipment with MS-gas detection allows the determination of vaporization of chemical reactive and toxic species such as halides, As_2O_3 , Na_2O , PbO etc. evolved out of the glass batch during the thermal treatment.

A possibility of production control by means of vacuum gas release profiles of glass-specimens is demonstrated.

Keywords: calorimetry, EGA, glass production

Introduction

The glass-forming process is a thermal process. In the more than 4.000 year long history of glass manufacturing, mankind has accumulated considerable empirical experience in the technique of manufacturing glasses for general and special use. Until today, however, the principles of these processes have remained comparatively poorly understood, with the consequence that most glassworks are highly dependent for their daily production on the individual skills of their glass-makers. Although thermal methods - especially DTA, DSC and dilatometry - have been widely used for the characterization of organic and inorganic glasses, they have not been extensively used for the investigation of the glass-forming process.

In fact, thermal methods are a powerful way of studying the glass-forming process, from the reaction of raw materials to the establishment of quality parameters for the final product, as well as for improving the conditions of

production with respect to their impact on the environment, energy consumption, the volume of production etc.

The efficiency of these methods has been fully accepted by, for instance, polymer scientists and engineers [1], but in 'classical' glass-making technology, these techniques do not appear to be widely used at present [2].

The classical papers by Wilburn [3] have demonstrated the usefulness of thermal investigations for the characterization of the glass-forming process, and Yamamoto discussed the use of DTA for the characterization of soda-lime-silica-glasses with respect to their thermal properties more than 20 years ago [4] without eliciting a significant response from the glass industry. One reason for the current situation may be the fact that the results of the 'classical' thermal analysis often fail to provide significantly useful information for the techniques of glass production (Fig. 1) [5].

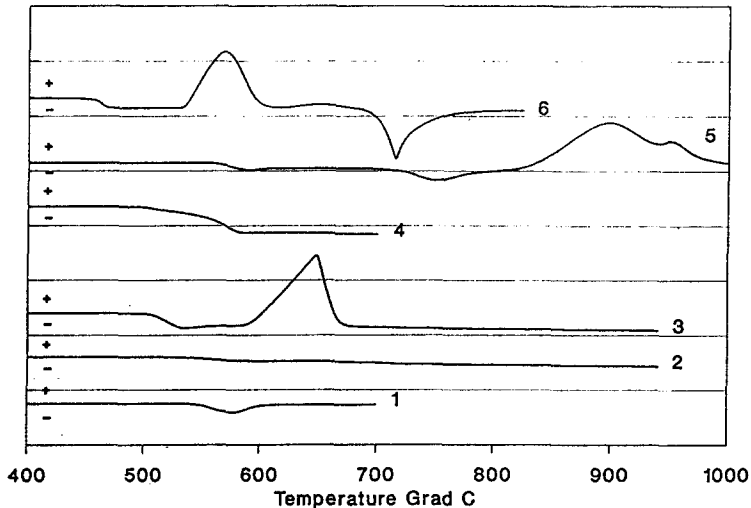


Fig. 1 DTA-curves for different glass types; 1 – optical silicate glass (spectacles glass); 2 – optical phosphate glass; 3 – Aegirine-glass ($\text{NaFeSi}_2\text{O}_8$); 4 – ICG-glass standard 'amber' (Na-Ca-Mg-silica-glass with sulfide); 5 – silicate glass ceramic before heat treatment; 6 – phosphate glass ceramic before heat treatment

The purpose of this paper is to discuss proposals for a modified thermal technique which takes into account the special problems of production and thermal behaviour of glasses.

Three aspects are of particular interest:

- The determination of the energy expended in the production of glasses;

- the determination of air-pollution and loss of raw materials as a result of the glass-making process, and
- the determination of thermal parameters of the final product as input for production control.

Determination of energy expended

The determination of energy expended in the glass-forming process is a problem of the measurement of heat-consumption as measurable by calorimeters. Two principles of calorimetric measurements are used: heat flux measurements and heat compensation [6]. In both cases, measurements require special conditions for the sample and its thermal treatment.

At temperatures from about 100°C to near 800°C, commercial power-compensated scanning calorimeters (DSC) can measure the heat of samples of 10–200 mg with an accuracy seldom better than 1%. Because measurements using DSC are usually taken at fairly rapid heating rates (1–10 deg/min) kinetic factors may influence the results.

In drop calorimetry techniques, the sample to be measured is thermally equilibrated in a furnace at some high temperature prior to dropping it into a calorimeter bath operated at low temperature. These measurements allow to determine the heat content $\Delta H_T - \Delta H_{298}$ directly.

Drop calorimetry is executed in the 100–1600°C range with a sample size of the order of 10 g. The maximum precision of such measurements is about 0.1%.

Both of these calorimetric techniques are quite different from the thermal treatment of a glass batch in a melting tank or melting crucible.

The ‘reversed-drop technique’ introduced in our laboratory – i.e. the ‘drop’ of a sample equilibrated at room temperature in a furnace at high temperature – is more similar to the thermal conditions operating when a glass batch is heated in a melting tank than the traditional methods.

Calorimetric measurements used for studies of the glass melting process must take into consideration the following special conditions, with respect to the constitution of a glass batch:

- the heterogeneity of the sample in the more than mm-scale (differences in the grain size of different raw materials and the culetts, lack of homogeneity in the distribution of components in the batch mixture);
- the large differences in the reaction kinetic of the different decomposition reaction, the rate of formation of intermediate and final phases, as well as the formation of partial or total melts;

– the packing density of particles, which strongly influences the kinetic of reactions.

No commercial apparatus exists at present which would allow an analysis of the heat content of such heterogeneous samples without a modification in the original constitution of the batch.

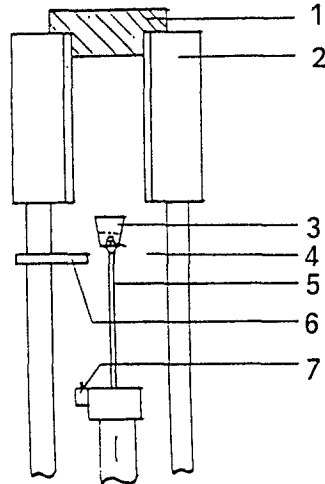


Fig. 2 Scheme of a 'reversed drop calorimeter' used for the determination of energy expended for the heating of a glass batch; 1 – cover plate; 2 – furnace; 3 – crucible with batch of glass; 4 – position of thermocouple; 5 – rod to hold the sample; 6 – brake and 7 – switch for the regulation of reproducible position of the sample

In Fig. 2 a scheme of a piece of an apparatus constructed in our laboratory for the determination of the heat content of glass batches of different composition in its original state is shown [7]. Compared to the commercial calorimeters, the accuracy of this method is quite low (about 5% maximum), but as is demonstrated in Fig. 3, the results do allow a first assessment of the influence of the substitution of batch components on the energy expended.

The results of calibration with a Seteram-high-temperature calorimeter for simple batches are summarized in Table 1.

The vaporization of raw materials and additives by thermal treatment of a glass batch

Conventional methods of evolved gas analysis have been widely described in the literature [5, 8, 9]. The vaporization of the glass batch by thermal treatment produces a lot of chemically reactive products such as Na_2O , PbO , borates, halides, As_2O_3 , and other fluid batch compounds. Determination of these volatile species by means of conventional EGA-systems is difficult, be-

cause of the condensation and reaction of the volatiles which occur in the apparatus.

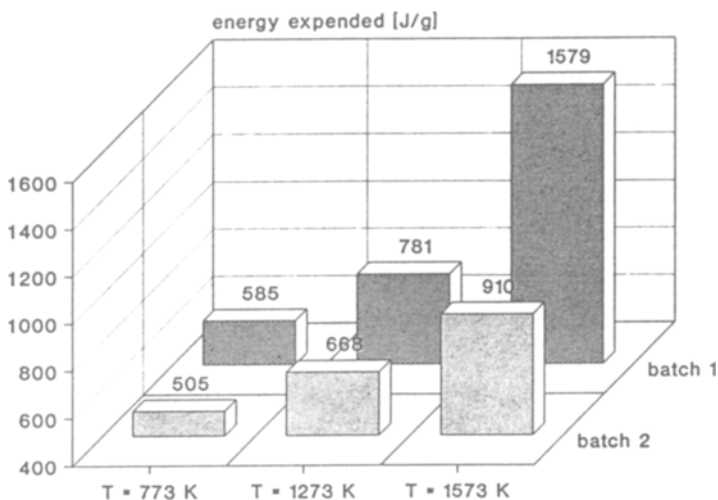


Fig. 3 Energy expended for the heating of glass batches without (batch 1) and with 40% cullets (batch 2)

Table 1 Calorimetric data for heating a glass batch, measured with self-made revers 'drop' calorimeter and a Seteram-high-temperature calorimeter (kJ/kg glas)

| Batch composition | Experimental data 309–1173 K | Seteram 298–1173 K | Theor. calc. [15] |
|---------------------------------|---------------------------------|-----------------------|----------------------|
| soda-silica powder | 1520 ± 60 | 1524 ± 15 | 1510 |
| soda-sand | 1220 ± 100 | 1549 ± 15 | 1510 |
| soda-Iceland spar-sand | 1594 ± 113 | | 1557 |
| soda-travertine-sand | 1245 ± 90 | | 1557 |
| soda-Iceland spar-silica powder | 1712 ± 108 | | 1557 |
| soda-travertine silica powder | 1703 ± 80 | | 1557 |

It will be seen that the different influence of kinetic factors by using both methods favours this modified method for using in industry.

The scheme in Fig. 4 shows how reactive volatiles may be determined under extreme non-equilibrium conditions. By means of these methods it has proved possible to determine the primary products of vaporization in the case of halide glass-formation [10, 11].

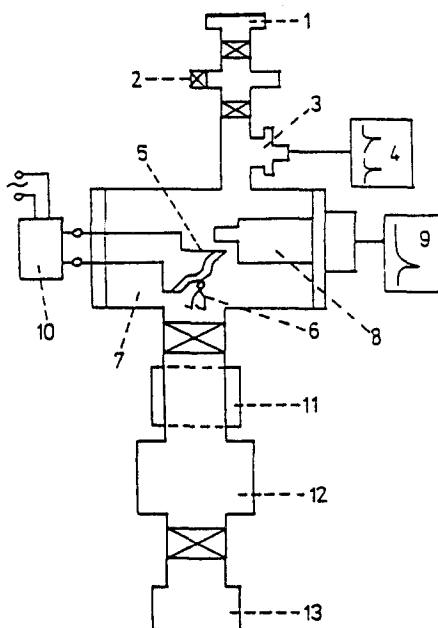


Fig. 4 Scheme of a system for the determination of chemically reactive volatiles produced by the thermal treatment of a glass batch; 1, 2 special inlet for bubble analysis; 3 total pressure gauge; 4 analog registration of the total pressure change; 5 sample device and furnace (distance between crucible and analyser approx. 2 cm); 6 thermocouple; 7 process chamber; 8 quadrupole mass spectrometer; 9 MS-registration; 10 regulation of heating rate; 11, 12, 13 high-vacuum system

There are HF, POF_3 and Al-F-H-species such as HALF_4 and Al_2F_6 , volatiles with a strong toxic effect. Furthermore, as an example it can be demonstrated in the case of the decomposition of monofluorophosphates that a formation of HF occurs primarily in a solid state reaction, and not by a hydrolysis of water vapour with the solid (Fig. 5).

The influence of the crystal structure on the species of the volatile is difficult to predict. In the case of borates and phosphates, the influence of the structural framework on the vaporization is quite small (Fig. 6) [12].

It has been proved possible by means of such investigations to establish the optimum conditions for producing halide glasses for high performance optics.

Gas-release profiles as a tool in production control

Any suggestions for improvement in glass-making performance require criteria for comparison. In practice, the quantity of bubbles in a volume of

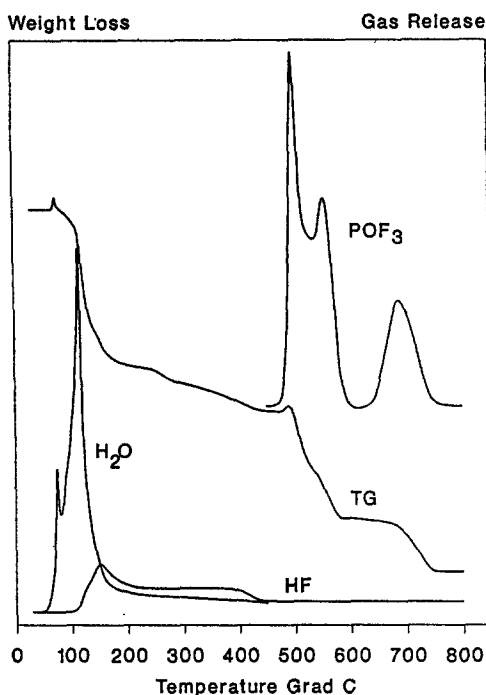


Fig. 5 Decomposition of $\text{SrPO}_3\text{F} \cdot \text{H}_2\text{O}$ in vacuum. The EGA shows that the formation of H_2O and HF is clearly separate from the formation of POF_3 ; sample weight: 14.3 mg; heating rate: 5 deg/min; crucible: Al_2O_3

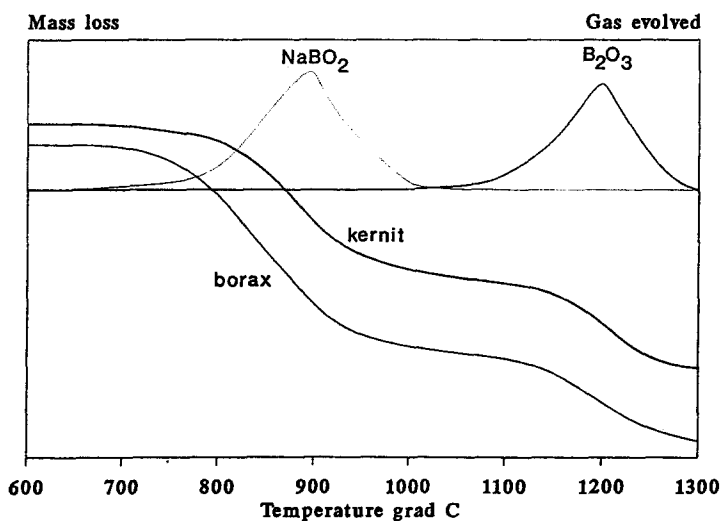


Fig. 6 The decomposition of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$) under high vacuum; sample weight: 10.0 mg; heating rate: 6 deg/min; crucible: Al_2O_3

glass provide such a criterion. There is a widespread agreement that the concentration of permanent gases in glass is a quantity which is in correlation with the bubble-frequency in the final product. It has been shown that this correlation is not simple and that there is considerable influence from a number of technological parameters. This means that no information on the quality of the final product can be derived from a determination of the total volume of gas solvent in the glass.

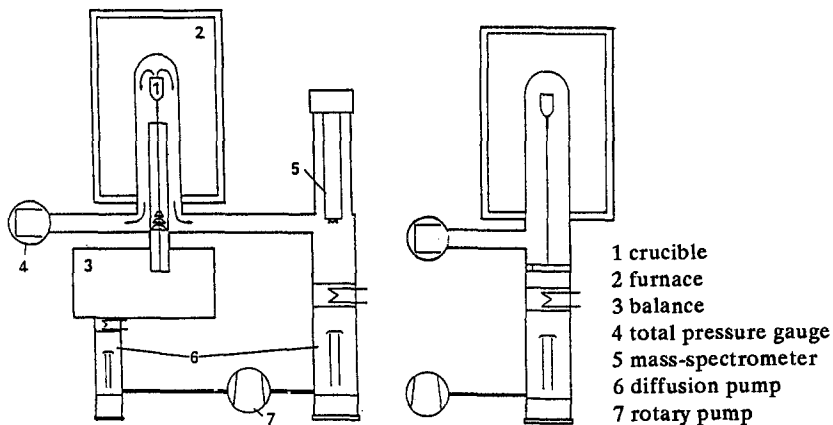


Fig. 7 Scheme of apparatus for determination of gas release profiles

It was shown [13, 14] that the gas-release profiles obtained from a modified EGA-equipment (Fig. 7) provide considerable information about the current situation in a melting tank. This information concerns both the 'fining state' and the 'fining behaviour' and the optimum temperature for handling the melt in respect to reboil-effects etc. (Fig. 8).

By means of such investigations, it is possible to establish for example the optimum concentration of fining agents such as As_2O_3 or the optimum temperature for the feeder of the melting tank. In this way it was possible to reduce the As_2O_3 -quantities in an optical glass batch and hence to improve the quality of the final product.

Conclusions

It was attempted to demonstrate by means of selected examples that thermal methods using the modifications to commercial equipments are a very useful tool for research and development in glass science and technology.

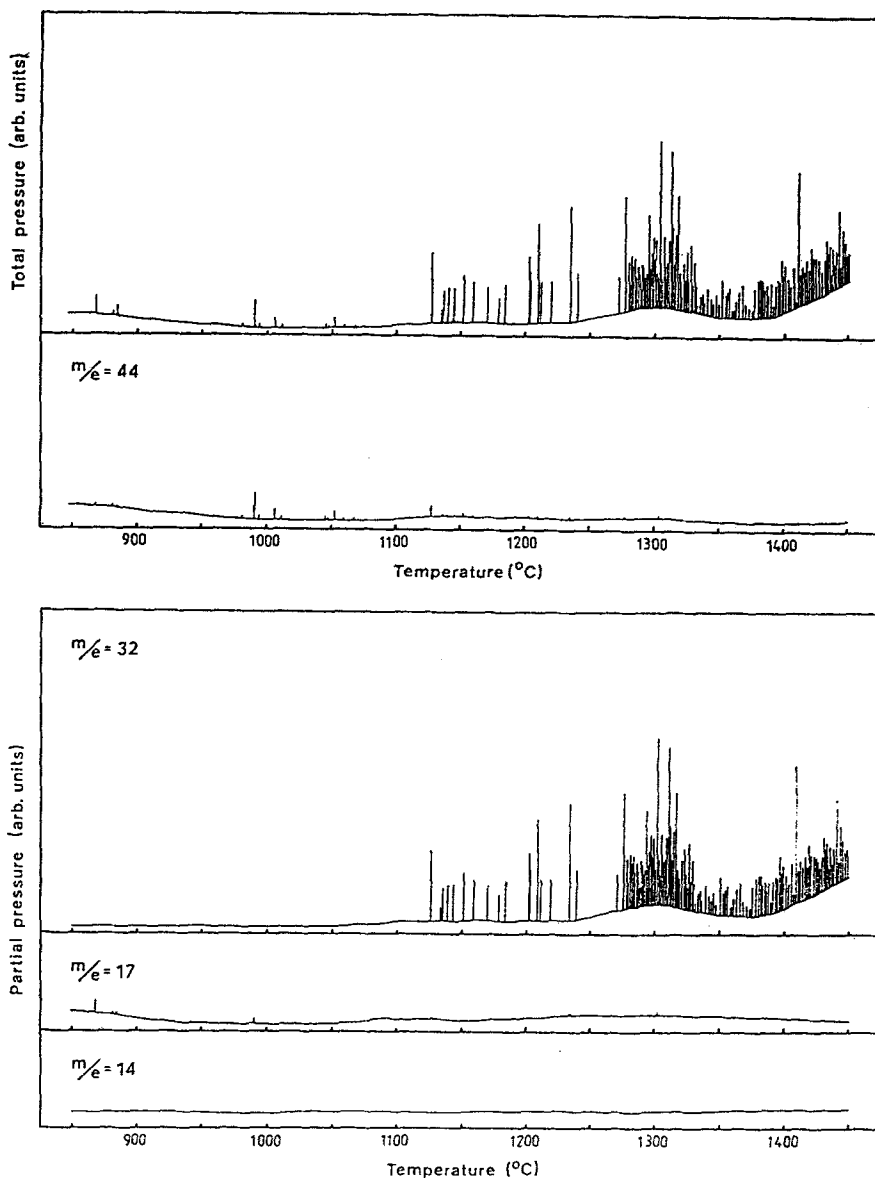


Fig. 8 Gas release profile of optical silicate glass with Sb_2O_3 for fining P = total pressure
 m/e 44 = CO_2^+ , m/e 32 = O_2 , m/e 17 = OH^+ (H_2O), m/e 14 = N^+ (N_2)

What is now required is the support by the producers of apparatus in order to control the environmental impact of a material which has proved of great im-

portance in our century, – a century which has, not without justification, been called the 'century of glass'.

At the same time, the glassmaker must also be ready in his turn to go beyond the traditional boundaries in the fields of production and quality control. But this is a topic of another publication.

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Zusammenfassung — Im Hinblick auf Steuerung und Optimierung der Glasherstellung wird die Möglichkeit von modifizierten thermoanalytischen Techniken diskutiert.

Besonders interessant sind Kalorimetrie und EGA-Messungen. Zur Bestimmung der Energie, die dafür benötigt wird, Glasgemenge thermisch in ihren ursprünglichen Beschaffheitszustand zu überführen, wird ein "umgekehrtes" Tropfenkalorimeter vorgestellt.

Eine spezielle EGA-Apparatur mit MS-Gasdetektion ermöglicht die Bestimmung der Verdampfung chemisch reaktiver und toxischer Substanzen wie z.B. von Halogeniden, As_2O_3 , Na_2O , PbO usw., die bei der Hitzebehandlung aus dem Glasgemenge austreten.

Es wird eine Möglichkeit zur Produktionssteuerung mit Hilfe der Gasprofile der in Vakuum freigesetzten Gase dargestellt.