

THERMOGRAVIMETRIC AND MASS SPECTROMETRIC INVESTIGATIONS OF THE DECOMPOSITION AND VOLATILIZATION OF RAW MATERIALS BY HEATING OF A GLASS BATCH

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The decomposition and volatilization reactions in the glass batch are important factors for the glass manufacturing, for the optimization of the melting conditions and material properties as well as for minimisation of the environmental impacts and complete utilisation of the raw materials. The use of modern analytical techniques to study such processes in laboratory is a first step towards industrial process control. One of the most successful techniques in evolved gas analysis has been the mass spectrometry.

The different types of mass filters and their advantages and limits are described for use in batch reactions and glass melting.

Secondly, the methods of interfacing for a simultaneous MS-analysis of decomposition and evaporation reactions under different conditions are discussed.

Thirdly, selected examples are given and discussed.

They include

- the control of decarbonatization of raw materials (soda, and calcite) by means of additives
- the evaporation of raw materials (boron) by heating of a glass batch
- the characterization of fining process of a glass melt
- the volatilization of fluorine, phosphorous and the formation of metal – gas – complexes by melting of fluoro-phosphate and fluoro-aluminate glasses.

The analysis of reactions in the glass batch by means of evolved gas analysis (EGA) was stimulated in the last ten years by the use of the modern analytical techniques of EGA, which allow the qualitative and quantitative measurements of vapour composition in connection with the heating process of the raw materials [1, 2].

The most successfully applied technique is mass spectrometry (MS) simultaneously with thermogravimetry and DTA. The use of MS to analyze evolved gases in general has been described in a number of papers [3, 5] but in most applied and described coupling systems the mass spectrometer fits directly into the vacuum system. The pressure during the reaction in this case must not exceed 10^{-4} torr, the pressure limit for the proportional relationship between ion current and sample concentration. For investigations in air or any other gas atmosphere under atmospheric pressure an interface for pressure reduction between the furnace and MS is necessary.

Different inlet systems have been described in literature [6–8] which should guarantee the

- unvaried gas composition
- short response time (time leak)
- no condensation effects of gases and vapours in the interface and
- no reactions of gases and vapours with material of the inlet system

The types of mass filters used are different.

When carried out simultaneously with TG, DSC, and/or DTA, MS provides a powerful method to investigate the thermal decomposition pattern of a material and to understand the reaction mechanism.

Experimental techniques

The basic principles of the three types of mass separation are indicated in the following.

In the magnetic sector field spectrometer (90 -degree mass spectrometer) the ions are separated according to their masses and electric charges (m/e) by a magnetic field. This analyzer in combination with a flexible inlet system permits the solution of numerous interesting problems of thermal degradation, e.g. the decomposition of polymeres and organic compounds, but also inorganic decomposition reactions.

Special advantages of this system are the high resolution ($R_{x\%}$) and sensitivity.

The resolution of a mass-spectrometer is defined by the ratio $R = m/\Delta m$ of the mass (m) to a distance expressed in (Δm), where m refers to the mass number at which the resolution is measured. Δm can be defined in different ways – the "10% valley" definition or with respect to peak width.

$$R_{x\%} = m/\Delta m_{x\%} = m/(a_{x\%}/b)$$

In the case of $R_{10\%} = 1200$ the resolution allows the separation of CO , N_2 and C_2H_4 with values of $m/e = 28.011$; 28.013 ; and 28.054 , respectively. Furthermore, the construction of multiple collectors allows a simultaneous determination of chosen gases in the original gas mixtures. Systems used in the steel industry (Fig 1) are, in principle, suitable for the automatic control of any thermal process.

But in the EGA such systems are not yet in common use. Many problems in this field may be solved by means of a much more economical system of mass-filter, as like the quadrupol mass spectrometers.

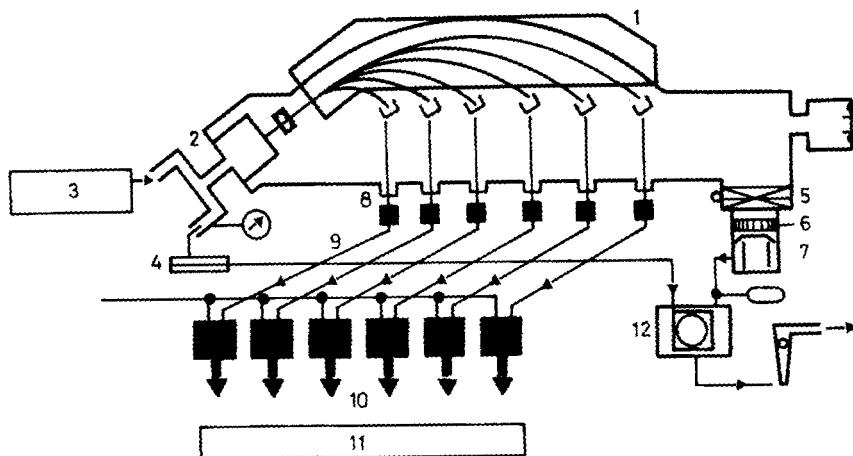


Fig. 1 Principle of a automatic control of steel production process by means of simultaneous gas analysis

1 – magnet, 2 – source, 3 – inlet of evolved gas, 4 – pressure regulator, 5 – gate valve, 6 – trap, 7 – diffusion pump, 8 – collection of separated masses, 9 – pre-amplifiers, 10 – outgoing electric signal, 11 – computer, 12 – rotary pump

The quadrupole mass spectrometer (QMG) operates on the principle of mass separation by ion oscillation in a high frequent electric quadrupole field. The stable ions, after passing the mass filter are detected by a Faraday cup collector or a secondary electron multiplier (SEM). The collector current, which is proportional to the partial pressure of the gas component in the ionizer is measured with an electrometer amplifier. The mass number of the ions which pass through the mass filter and are collected is proportional to the amplitude V .

The resolution is specified in terms of one mass-unit, that means as 28 at the mass 28 or 100 at mass 100 ("10% valley" definition, $\Delta m = 1$).

The separation of CO , N_2 , C_2H_4 ($m/e = 28$) is possible only by using the determination of the fragments of molecule ions (Fig. 2). Units designed for connection to data processing equipments allow the interpretation of single mass lines or mass groups sufficiently reliably and quickly. Removal of all the gaseous decomposition products into the mass spectrometer is best achieved by placing the sample within the analyzer system itself.

The earliest construction heated the sample in a miniature furnace within the ion source of a time-of-flight mass spectrometer.

Systems of these types have the advantage that, due to the short sample-analyzer distance involved, secondary reactions and vapour sublimation are minimised.

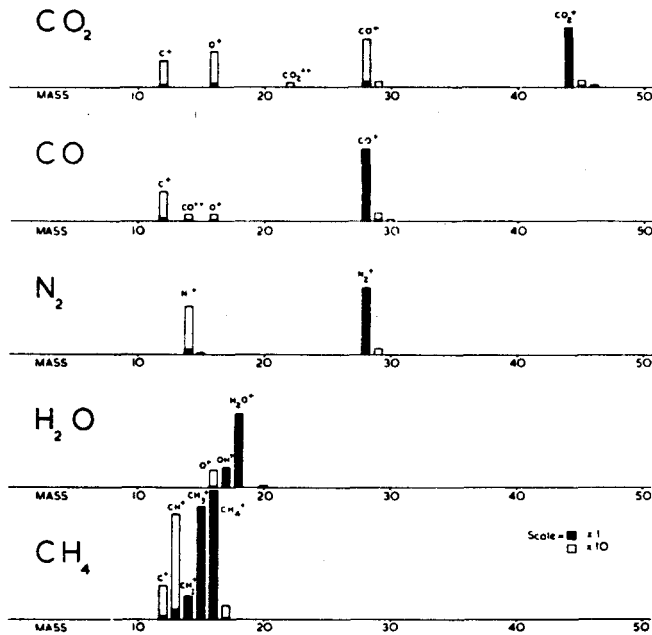


Fig. 2 Fragmentation of molecules by ionization in the ion source of mass-spectrometer

The operating principle of these time-of-flight mass spectrometers is the ionization of the gases by an electron beam, formation in a drift tube, formation of packets of accelerated ions with equal mass-charge ratios, and display of ion current by means of a broadband oscilloscope system. This type of mass spectrometer is especially suitable for studying and measuring fast gas dynamic processes in vacuum under nonsteady-state conditions (e.g. explosions).

For the investigation of reactions in the glass batch and the volatilization of components from the batch and during the melting as well as for the determination of gas content in the final product of glass making use of a quadrupole mass spectrometer was extremely helpful. The QMS used in this study has different coupling and inlet systems for a simultaneous TA-QMS-analysis.

Figure 3 shows an experimental set-up for investigations of decomposition of raw materials in a glass batch in control atmosphere conditions. The maximum temperature is 1600°.

The two-step decomposition of dolomite provides a good example of demonstration of the short dead time as shown in Fig. 4.

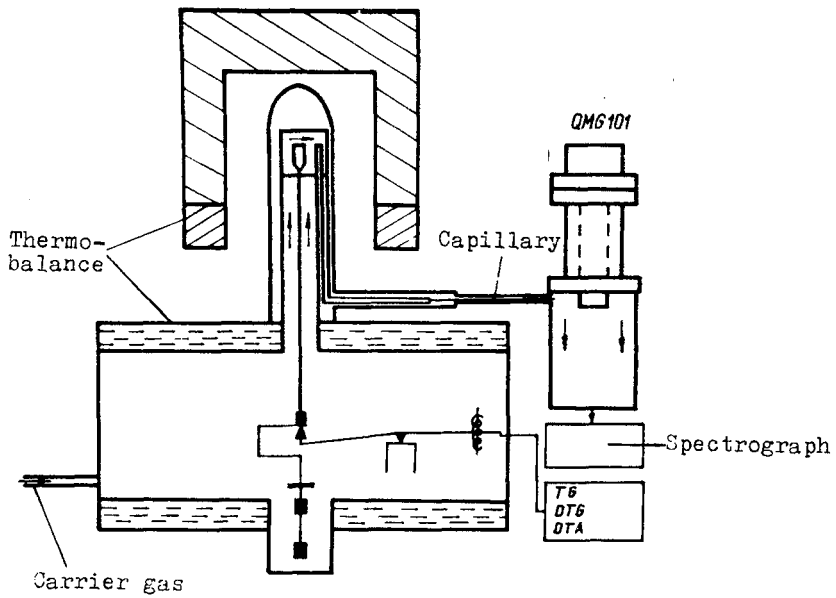


Fig. 3 Principle of the coupling of a thermobalance with MS by a capillary

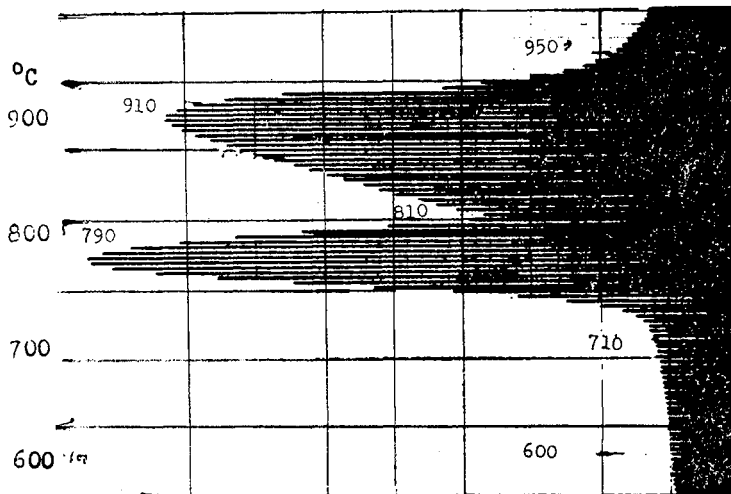


Fig. 4 The MS-analysis of decomposition of dolomite under atmospheric pressure, showing the evolution of CO_2 , sample weight: 100 mg; heating rate: 10 deg/min; carrier gas: argon 8 l/h; crucible: Pt (Mettler-standard); temperature measurement: on the bottom of the crucible.

As we can show on the basis of first results it is possible to determine the change in the partial pressure under atmospheric pressure by means of an inlet system as in Fig. 5.

The bursting of the bubbles produces a spontaneous increase in the partial pressure and it is possible to determine the fining temperature and the fining time without difficulties (Fig. 6).

The determination of degassing behaviour of glasses is a further aspect of the use of MS-gas analysis. The MS-analysis of gas content and the degassing behaviour of glasses can be carried out by placing the sample directly into the vacuum system (Fig. 7). The sample size depends on the degassing rate and total gas volume and in general is only some milligrams.

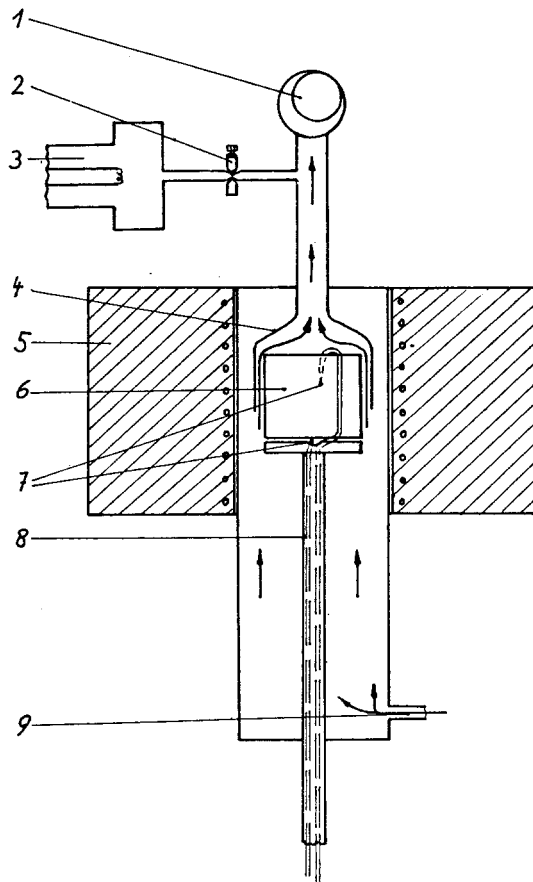


Fig. 5 System for investigation of glass melting
 1 – rotation pump, 2 – inlet with damp, 3 – spectrometer, 4 – outlet, 5 – oven, 6 – crucible,
 7 – thermocouple, 8 – crucible holder, 9 – carrier gas

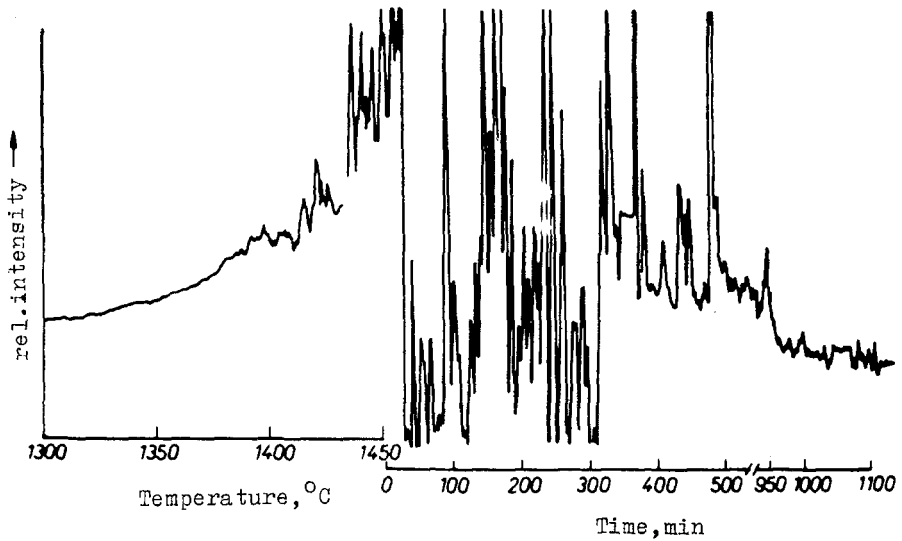


Fig. 6 The degasing of O_2 of a glass melt under atmospheric pressure. (Sample weight: 1500 mg; heating rate up to $1450^\circ C$: 10 deg/min, carrier gas: argon 8 l/h, crucible: Al_2O_3 ; temperature measurement: on the bottom of the crucible)

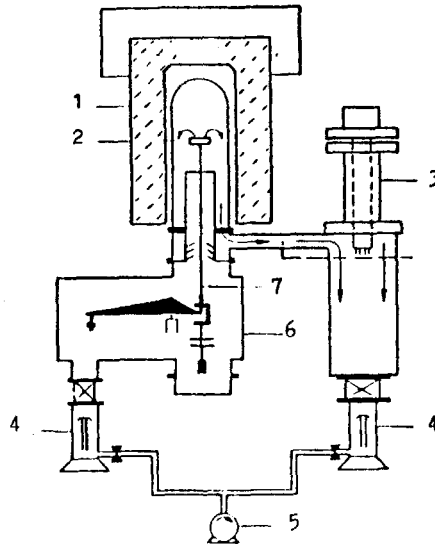


Fig. 7. QMS analyzer attached to TA vacuum system
1 – furnace, 2 – crucible, 3 – mass-spectrometer, 4 – diffusion pump, 5 – rotary pump, 6 – balance, 7 – sample holder

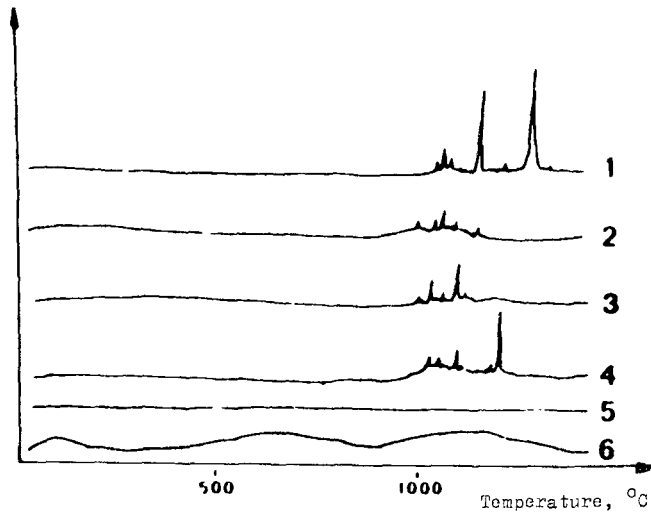


Fig. 8 Degassing behaviour of a container glass; m/e values: 1 – 32; 2 – 64; 3 – 12; 4 – 44; 5 – 14; 6 – 18.

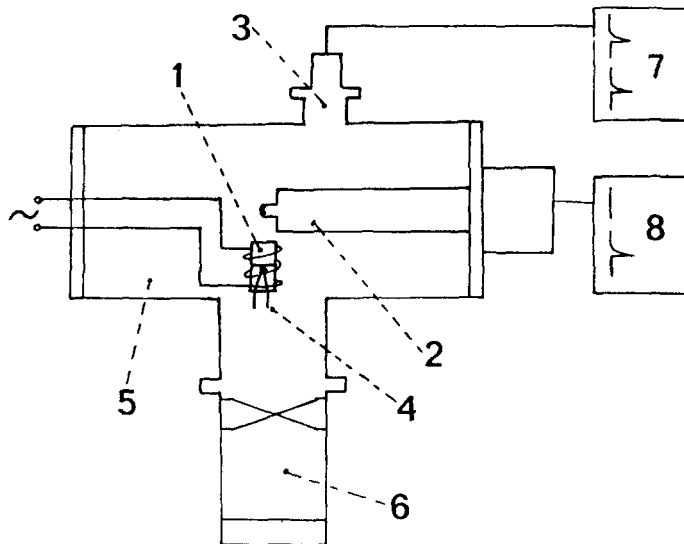


Fig. 9 Experimental set-up of a Knudsen cell / MS coupling.

1 – micro-furnace, 2 – MS-analyzer, 3 – total pressure gauge, 4 – thermocouple, 5 – recipient, 6 – diffusion pump, 7 – total pressure measurement, 8 – partial pressure measurement

By means of such investigations we can observe that rate of volatilization and the temperature of forming of bubbles is different for different kinds of volatiles. (Fig. 8)

These figures allow statements concerning the origin and the initial products of the vitreous body.

Limitations of this method result from condensation effects of gases and vapours. The heating of inlet system and spectrometer is limited and the interpretation of results is quite difficult in this case.

From Knudsen cell experiments a complete evidence of volatile compounds should be expected, if the distance between the sample and ion source is minimized (that means < 2 cm). For such applications, an arrangement of microfurnace at temperatures up to 1250° together with a Knudsen cell according to Figs. 9 and 10 has to be used. But we must take into consideration that the results give information about the vapor equilibrium in the cell which contains also secondary reaction products formed by molecule reactions, wall collisions or catalytically induced reactions.

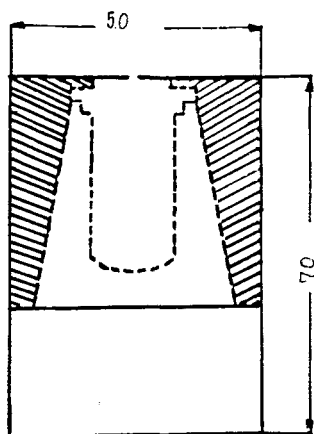


Fig. 10 Pt-Knudsen cell; lined part: Pt-cover with orifice (mm)

Experimental results and discussion

The decomposition of raw materials gives information about the temperature range and rate of chemical processes in a glass batch, in particular about the influence of fining agents and other admixtures.

Presented in Fig. 11 are the DTG/MS curves which were recorded during the investigation of raw material mixtures with different contents of sodium nitrate by heating under atmospheric pressure. These curves show

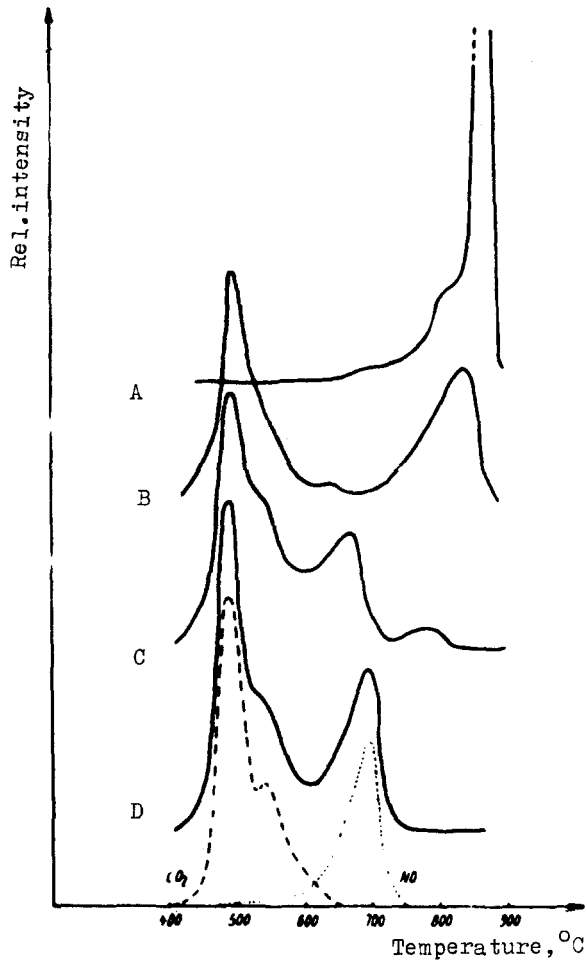
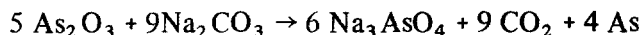
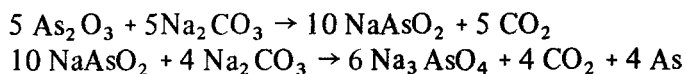
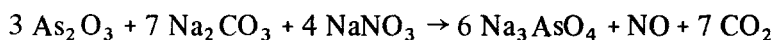
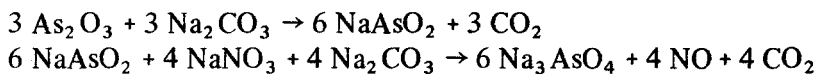


Fig. 11 The decomposition of a batch ($\text{Na}_2\text{CO}_3\text{-SiO}_2$) in dependence of the concentration of NaNO_3 .
 --- DTG-curves
 --- MS-curve $m/e = 44$
 ... MS-curve $m/e = 30$
 A— $\text{Na}_2\text{CO}_3 + \text{SiO}_2$, B—+0.9 mol% NaNO_3 , C—+2.3 mol% NaNO_3 , D—+4.5 mol% NaNO_3

that the decomposition of caustic soda is changed strongly by addition of NaNO_3 . In the practice of the glassmaking process we know that the addition of NaNO_3 to the fining agent As_2O_3 minimizes arsenic evaporation effectively. The volatilization of arsenic is under control of the formation of sodium meta-arsenate:



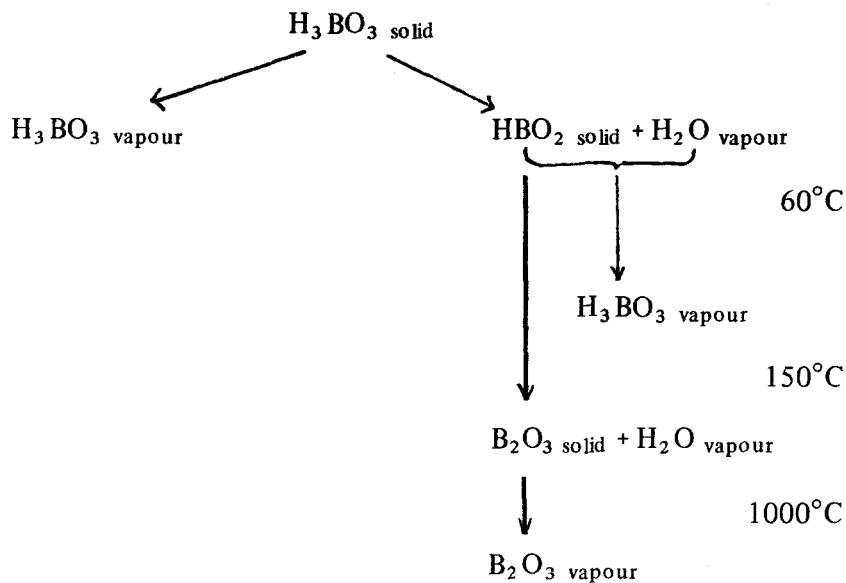
and



The oxidation of metallic arsenic is effected by means of the addition of NaNO_3 .

The volatilization of additives has a strong economic and environmental effect.

In case of boron acid, a simultaneous evaporation, decomposition and formation of boron acid by heating were observed. The mass loss through volatilization is determined by the reaction time of water vapour with the residual decomposition products (e.g. in case of boron acid H_3BO_3 meta-boron acid HBO_2):



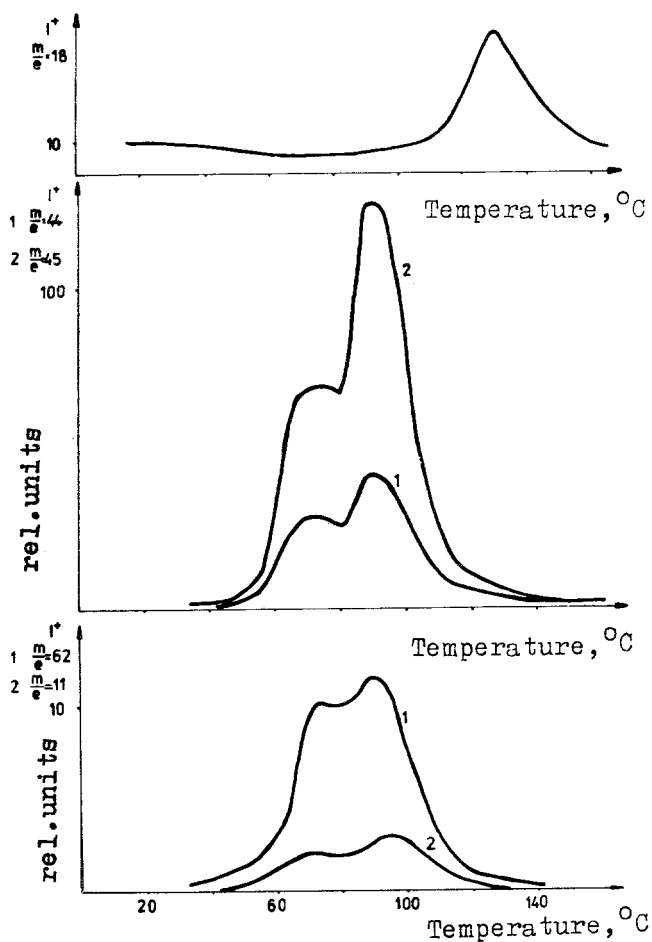


Fig. 12 The volatilization of H_3BO_3 (MS-investigation)

The volatile phases are water vapor and orthoboron acid as we can show by MS- analysis [1].

More complicated is the volatilization in systems with fluorine and phosphorus – glass batches which are of special interest for the production of optical special glasses.

In this case the formation of POF_3 and much more complicated gas complexes can be observed together with HF and AlF_3 like $HAIF_4$ in the phase by heating of a batch in fluoride – phosphate systems [10].

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Zusammenfassung – Zersetzungs- und Verdampfungsreaktionen im Glasgemenge sind bedeutende Faktoren für die Glasherstellung, für die Optimierung der Schmelzbedingungen und Materialeigenschaften als auch für eine Minimalisierung von Umgebungseinflüssen und eine vollständige Nutzung der Rohstoffe. Die Anwendung moderner analytischer Methoden zur Untersuchung solcher Prozesse unter Laborbedingungen stellt einen ersten Schritt zur industriellen Fertigungsüberwachung dar. Eins der erfolgreichsten Verfahren zur Untersuchung der entstehenden Gase ist die Massenspektrometrie.

Es wurden die verschiedenen Arten von Analysatoren sowie deren Vorteile und Begrenztheit für die Anwendung in Glasgemengereaktionen und beim Glasschmelzen beschrieben.

Weiterhin wurden Methoden zur Verbindung einer simultanen MS-Analyse von Zersetzungs- und Verdampfungsreaktionen unter verschiedenen Bedingungen besprochen.

Letztendlich wurden ausgewählte Beispiele dargestellt und besprochen, die folgendes umfassen:

- Überwachung des Austreibens von Kohlendioxid aus Rohstoffen (Soda, Kalzit) mittels Zusätzen.
- Verdampfen von Rohstoffen (Bor) durch Erhitzen des Glasgemenges.
- Kennzeichnung des Läuterungsprozesses einer Glasschmelze.
- Verdampfen von Fluor, Phosphor und Bildung von Metall-Glass-Komplexen beim Schmelzen von Fluorophosphat- und Fluoraluminatglas.

Резюме – Происходящие в стекольной ванне реакции разложения и испарения являются важными факторами в производстве стекла, оптимизации условий плавления и свойств веществ, а также в уменьшении до минимума влияния внешних воздействий и полного использования сырья. Использование современных аналитических методов для изучения таких процессов в лабораторных условиях, является первым шагом в контроле промышленного процесса. Масс-спектрометрия была использована как один из наиболее приемлемых методов в анализе выделяющегося газа. Описаны преимущества и недостатки различных масс-фильтров, используемых

в реакционных ваннах и при плавлении стекла. Обсуждены методы, позволяющие совмещать масс-спектральный анализ реакций разложения и испарения, проводимых в различных условиях. Приведены и обсуждены отдельные примеры, включающие контроль обезуглероживания сырья / сода и кальцит / путем введения добавок, испарение бора путем нагревания стекольной ванны, характеристика конечного процесса стеклоплава, испарение фтора, фосфора и образование металл - газ комплексов при плавлении фторофосфатных и фтороалюминатных стекол.