

QUANTITATIVE EGA ANALYSIS OF H₂O IN SILICATE GLASSES

D. Schöps*, C. M. Schmidt and K. Heide

Friedrich-Schiller-University Jena, Institute for Geosciences, Burgweg 11, 07749 Jena, Germany

The properties and quality of silicate glasses strongly depend on the amount of residual dissolved gases. Thus, the knowledge of the quantitative content of different volatile components is of great relevance within the technical production line. Several applications exist for the detection and quantification of a single gas in glass. Up to now no available technique provides simultaneous and quantitative information on different gases in a single run. We have developed a new technique to detect the most common volatiles (H₂O, CO₂, SO₂, O₂ and N₂) simultaneously and quantitatively in silicate glasses with the help of a modified Netzsch TG/MS system. One characteristic feature of this new method is the direct coupling of a thermo balance and a mass spectrometer without the use of any capillary or skimmer system.

Keywords: DEGAS, gas analysis, glass, reference material, TG/MS

Introduction

Dissolved and chemically bound gases such as H₂O, CO₂, SO₂, O₂, N₂ and others are able to influence considerably the physical and chemical properties of silicate melts [1, 2]. Thus, the knowledge of the quantitative content of these gases is of great interest for the glass producing industry as well as for geoscientists who are studying the volatile components of natural glasses and rocks. Up to the present no available technique allows the simultaneous and quantitative measurements of different gases in a single run. As an example, there exists several methods to detect H₂O in a sample: infrared spectroscopy (IR), Karl–Fischer titration (KFT) and, more recently, nuclear reaction analysis (NRA) and Raman spectroscopy are able to detect bulk H₂O, whereas secondary ion mass spectrometry (SIMS) and micro-Fourier transform infrared spectroscopy (μ -FTIR) are micro-analytical techniques. None of these techniques is able to detect other gases of relevance in the same run so that, as a consequence, additional analytical equipment is necessary. For small and medium-sized glass plants and research institutions the acquisition and maintenance of such an analytical pool is beyond their financial possibilities. For this reason, the Institute for Geoscience at the Friedrich-Schiller-University Jena (Germany) has developed an analytical system to detect and quantify different gas phases simultaneously and quantitatively in a single run. In the present paper we describe our new method, the instrument behind this method and our first experiences with the calibration of water.

Experimental

Method

To detect released gas fragments up to a mass of $m/z=200$ in silicate melts we use a commercial, slightly modified Netzsch TG/MS system (Fig. 1). One characteristic feature of this instrument is the direct coupling of the thermobalance and the mass spectrometer without the use of any capillary or skimmer system. This new method is called DEGAS – directly coupled evolved gas analysing system. A more detailed description of the instrument is given in [3].

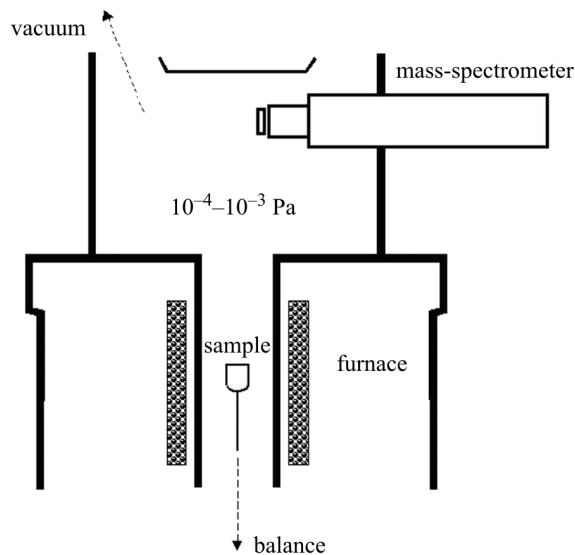


Fig. 1 Schematic sketch of the DEGAS system at Friedrich-Schiller-University, Jena

* Author for correspondence: Dietmar.Schoeps@uni-jena.de

Combined TG/MS techniques have been widely used for the simultaneous and quantitative detection of inorganic and organic compounds during heating [4, 5]. One major problem of these methods is the possibility of reverse reactions of evolved volatile components. Vacuum pyrolysis combined with direct mass spectrometric detection (no pressure reduction!) has the advantage of operating at highly non-equilibrated conditions. Thus, intensive reverse reactions can be avoided considerably. In addition, due to a reduced distance of the crucible and the MS detector to about 15 cm the condensation of volatiles inside the coupling system will be largely prevented.

Within the vacuum chamber a multiple crucible sample holder (Fig. 2) allows the use of an internal reference sample without direct contact of sample and reference material (500 μL sample crucible and 20 μL reference crucible). For running calibrations up to four small crucibles (20 μL) can be placed on the sample holder. The distance between sample holder and mass spectrometer is less than 20 cm, the vacuum is in the range of 10^{-4} to 10^{-3} Pa. Volatiles (permanent gases and evaporation products) are liberated from the glass or rock samples by bubbling and diffusion processes during heating up to 1450°C with a rate of 10 K min^{-1} . Depending on the amount of a volatile component in a given sample in most cases less than 100 mg are needed to detect the gas by the mass spectrometer. Gas rich samples require only a few milligrams to get an excellent release pattern.

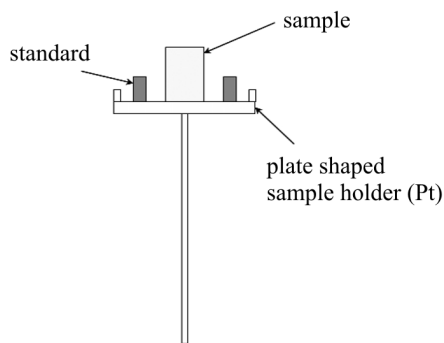


Fig. 2 Schematic sketch of the multiple crucible sample holder

Schmidt and Heide [6] have shown that – under standardized conditions – using DEGAS the reproducibility of measurements is below 5%.

Calibration procedure and reference material

To calibrate the instrument for quantitative measurements of different volatile components it is necessary to record the thermal decomposition of a reference material by its MS signal (Fig. 3). By weighing different amounts of a reference material (0.1...10 mg) we

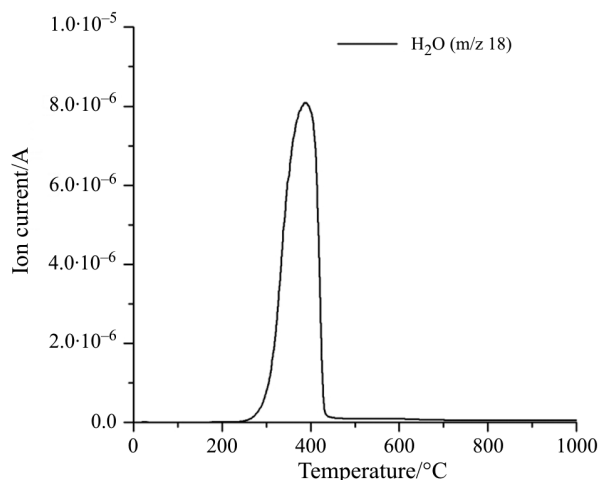


Fig. 3 Thermal decomposition pattern of brucite $\text{Mg}(\text{OH})_2$ with maximum release of water at around 400°C

detect the decomposition signal and relate the recorded peak area to the certified amount of released gas (Fig. 4). As certified reference material is sometimes extremely expensive and even not available for all volatile components we want to detect the idea is to use pure natural minerals such as e.g. gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcite (CaCO_3) and hematite (Fe_2O_3) as reference material. In this way we are able to receive H_2O , CO_2 , SO_2 and O_2 decomposition signals from low-cost material. Available as single crystals the above-mentioned minerals have the great advantage to be of stoichiometric composition and thus exactly match the theoretically given volatile content (Table 1). Before using the minerals as reference materials they have to be checked carefully by mineralogical means for purity.

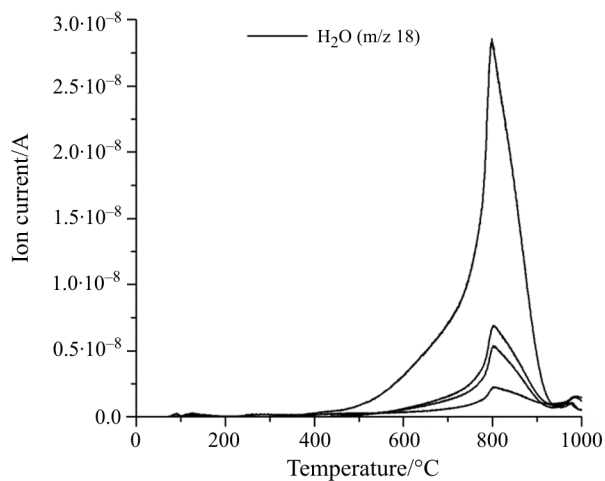


Fig. 4 Typical thermal dehydration patterns of an interlaboratory muscovite $\text{KAl}_2[(\text{OH})_2/(\text{AlSi}_3\text{O}_{10})]$ standard at around 800°C with different mass of material (0.3, 0.9, 1.2 and 6.0 mg, respectively)

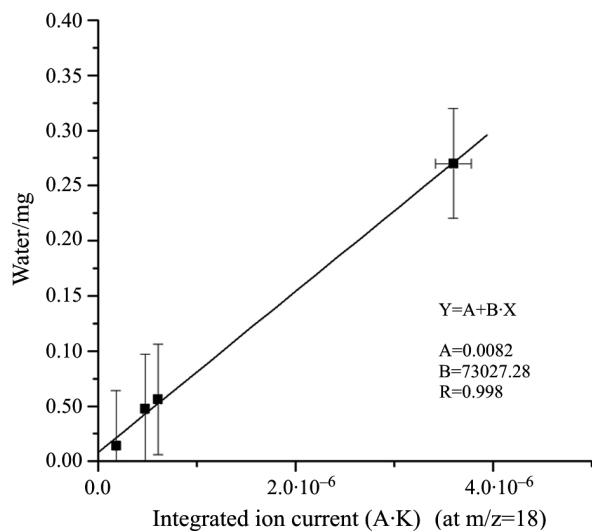
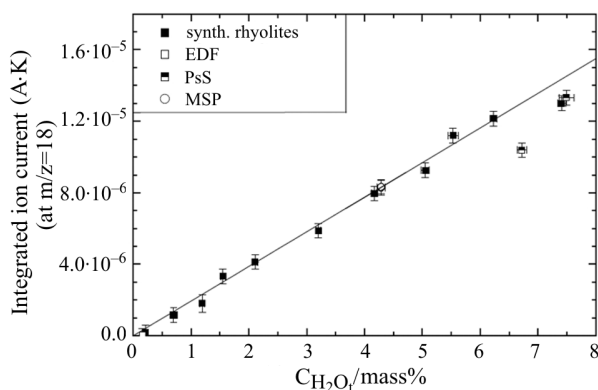
Table 1 List of suitable reference materials for the calibration of H₂O, CO₂, SO₂ and O₂ of the DEGAS instrument with their chemical formula and volatile contents

Analyte	Reference material	Formula	Volatile content/ <i>m/m%</i>
H ₂ O	gypsum	CaSO ₄ ·2H ₂ O	20.9 – H ₂ O
	kieserite	MgSO ₄ ·H ₂ O	13.0 – H ₂ O
CO ₂	calcite	CaCO ₃	44.0 – CO ₂
	witherite	BaCO ₃	22.3 – CO ₂
SO ₂	gypsum	CaSO ₄ ·2H ₂ O	46.5 – SO ₃
	anhydrite	CaSO ₄	58.8 – SO ₃
O ₂	hematite	Fe ₂ O ₃	30.0 – O ₂
	magnetite	Fe ₃ O ₄	27.6 – O ₂

In case of water calibration with gypsum we use maria-glass as reference mineral. Maria-glass is a transparent variety of gypsum and contains definitely two moles of water per formula unit corresponding to 20.9 mass% H₂O. No hemi-hydrate phases exist for maria-glass. In addition, the release of exactly two moles of water is checked by simultaneous thermogravimetric detection during the calibration run.

Further studies will deal with the calibration of nitrogen. In the case of N₂ natural stoichiometric minerals are extremely rare and are not suitable for heating experiments. For this reason thermal decomposition of synthetic nitrides and organic compounds will be carried out in the next future.

As an example for the successful calibration of H₂O Fig. 5 shows the calibration plot of the integrated MS signal resulting from the decomposition of a standard muscovite KAl₂[(OH)₂/(AlSi₃O₁₀)] vs. the released amount of water in mg.


Fig. 5 H₂O calibration plot using DEGAS showing the integrated MS signal vs. the released amount of water coming from the decomposition of the standard muscovite

Fig. 6 Comparison of the water content of different minerals and rocks analysed by Karl–Fischer titration ($C_{H_2O_1}$) vs. the integrated MS signal for $m/z=18$ (H₂O) of the same material. Figure from [7]. MSP=muscovite from Spittal (Austria), PsS=pitchstone from Saxony (Germany), EDF=obsidian from Erevan Dry Fountain (Armenia), synth. rhyolite=synthetically molten SiO₂-rich rock

To check our calibration obtained from standard muscovite we measured a large amount of water bearing samples, calculated the peak area of released water during heating and plot this against the concentration of water measured by conventional Karl–Fischer titration (KFT) (Fig. 6). The resulting diagram shows a linear regression over a wide range of the water content. Difficulties arise from samples with >6 mass% H₂O. Here, the water content measured by DEGAS is lower than obtained by KFT. This phenomenon might be due to the easily loss of highly water-bearing samples during vacuum pumping. However, in normal glass production processes such a high water content will usually not occur.

Future developments of measurements will carry one or more small splits of an internal reference material together with the analysing material in the sample holder. This procedure requires different degassing temperatures of the sample and the reference material that has to be checked prior to the final measurement. Another possibility is to expose several reference materials with different degassing temperatures on the sample holder. This will shorten the time of calibration considerably.

Conclusions

With the development of the new DEGAS method we are able to detect simultaneously and quantitatively a large number of gases relevant in glass production and geochemistry. Fragment ions up to a mass of $m/z=200$ of the released gas can be detected during heating the sample up to 1450°C. This time and temperature resolved measurement allows the simultaneous detection of different species. In addition, a simultaneous detec-

tion of the mass loss of the sample is possible by thermogravimetric control. An additional advantage of our method is that there is no special sample preparation necessary to detect all relevant components. Depending on the amount of gases in the glass (or rock) only a few milligrams of sample are required for detection. Calibration measurements show a linear regression over several units (mg kg^{-1} to mass%) and a matrix dependence was not found in our experiments.

It has been shown that DEGAS is an efficient and powerful tool to detect quantitatively the amount of relevant gases in glasses and rocks. At present, DEGAS has been calibrated and successfully tested for the quantitative detection of H_2O . In the near future we will broaden the spectrum of relevant species to CO_2 , SO_2 , O_2 and N_2 .

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