Using a Carbon/Sulphur Analyser (multi EA® 4000) in the Glass Industry

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In glass production, the total sulphur parameter is particularly important when it comes to quality assurance. The sulphur content is calculated as the SO_3 content and provides important information about the quality, stability and usability of the glass.

In the production of foam glass, which is used as insulating material, the determination of total sulphur is important. The carbon content of the starting material (carbon black/glass mixture) provides information about the expected insulating properties of the finished product and is therefore of major importance for quality assurance.

Introduction

Analysers for the determination of carbon and sulphur in solid materials, such as the multi EA® 4000, are used in different fields of industry, and for environmental and research applications. Whenever it comes to quality control, the total carbon (TC) and total sulphur (TS) parameters play an important role. In the cement industry, for example, the TC and the TS are not only determined from the raw product (clinker, raw cement), but also from secondary fuels which are needed to produce energy in cement production. The multi EA® 4000 is also of great importance for waste incineration plants. Here, the total carbon and total sulphur parameters are not only determined from the starting material (waste). The carbon and sulphur content of the incineration residue (slag) is also important for the material's suitability for landfill disposal.

Determination of sulphur in the glass industry

When using elemental analysers in the glass industry, not only the TC parameter is of interest, but also the TS parameter. In glass production (soda-lime glass), the raw materials silica sand (SiO_2), lime ($CaCO_3$) and soda (Na_2CO_3), in particular, are used. This mixture melts at approx. 1200°C and this leads to the formation of carbon dioxide bubbles (CO_2).

$$SiO_2 \cdot CaCO_3 \cdot Na_2CO_3 \rightarrow SiO_2 \cdot CaO \cdot Na_2O + 2\ CO_2\uparrow$$

To improve the thorough mixing of the viscous mass, gases are additionally blown in (bubbling), creating a type of foam. However, the high viscosity of the molten glass prevents the gas bubbles from being completely discharged. This is necessary because otherwise gas inclusions may form during cooling and reduce the quality of the glass. To remove the gas bubbles from the mixture, a refining (cleaning) process is used. In this process, sodium sulphate (Na_2SO_4) is additionally added to the melt, which decomposes to form gaseous sulphur dioxide (SO_2).

$$2\ SiO_2 + 2\ Na_2SO_4 \rightarrow 2\ SiO_2 \cdot Na_2O + 2\ SO_2\uparrow + O_2$$

On rising, the SO_2 transports further gaseous constituents of the molten glass, thereby improving the quality of the glass. However, the proportion of Na_2SO_4 plays a major role. If too much is added to the mixture, pools of liquid sulphur trioxide (SO_3) will form during cooling, making the glass brittle.

$$Na_2SO_4 \rightarrow Na_2O + SO_3$$

Manufacturers therefore define limits for SO_3 in the finished glass to control and maintain the quality of their products. Using the multi EA® 4000 it is possible to determine the sulphur content within minutes and easily convert it to the SO_3 content.

$$SO_3 = TS \cdot \frac{M(SO_3)}{M(S)} \approx TS \cdot 2{,}50$$

Determination of carbon in the glass industry

In contrast to the widespread use of sulphur analysis, the determination of the carbon content in glass is considered a special application. The above-described effect where the presence of CO_2 in glass production can lead to a reduction in quality can also be exploited for the production of foam glass. Foam glass is a porous material with a large surface area and has outstanding insulation properties. Unlike other insulation materials, foam glass is long-time stable and can be recycled. For production, the starting materials together with recycled glass are ground into a fine powder in ball mills. Elemental carbon in the form of carbon black is then added to the initial mixture to obtain as many gas bubbles as possible in the melt through the formation of CO_2.

$$C + O_2 \rightarrow CO_2\uparrow$$

If the glass solidifies on cooling, the gaseous inclusions remain behind, thereby creating the insulating effect of the foam glass. However, the proportion of carbon is decisive for the quality of the foam glass. If there is too little carbon, too few bubbles are formed, with the result that the glass is not porous enough for use as an insulating material. Too much carbon, on the other hand, produces, similar to the refining process, too many and too large bubbles, which are discharged from the melt. This also results in a reduced porosity. It is therefore important to still determine the TC of the initial mixture before the melt to guarantee a consistent quality at the end. The multi EA® 4000 with its high temperature digestion is also used for this application to analyse the quality of the mixture in a short time.

Instrumentation

For the determination of the TC or TS parameters, the elemental analytical system multi EA® 4000 was used in combination with the automatic sampler FPG 48 *(see Figure 1)*. The detection of the SO_2 and CO_2 gas which was formed during determination was carried out using NDIR spectrometry, a well proven and also selective measuring principle.

Figure 1. multi EA® 4000 (without FPG 48)

Calibration

Before actual sample measurement, the multi EA® 4000 must be calibrated using suitable materials. This requires that matrix-related standards should be used for calibration if possible. For TS calibration, a glass standard from the "Deutsche Glasgesellschaft" (DGG) (German glass society) with a defined amount of sulphur (0.1744%, equivalent to 0.4355% SO_3) was used. For TC calibration, no commercially available glass standards are available. For this reason, a ready glass/carbon black mixture with a defined amount of carbon black (0.317%) was prepared.

Sample measurement

For the determination of total sulphur in different glasses, the use of additives is necessary to ensure complete sample digestion. The additives were selected in accordance with DIN 51085. To ensure complete digestion of the glasses, elemental tungsten and tin was mixed in a ratio of 1 to 1. These react with the constituents of the glass to ensure the complete reaction of all sulphur compounds in the glass. To enable homogeneous heating of the glasses, it is necessary to cover the sample with iron filings. The sample preparation procedure was performed both for calibration and for the glass samples. Subsequent digestion was performed at 1350°C in an oxygen stream. The results of the measurements are summarised in *Table 1*.

Table 1. Results of the TS measurement of different glasses

Sample name	Sulphur content in %	SO_3 content in %
Sample 1	0.09 ± 0.005	0.22
Sample 2	0.05 ± 0.005	0.13
Sample 3	0.02 ± 0.005	0.05

The graphical course of a TS measurement is shown in *Figure 2*. It can be seen that digestion was complete because the curve already reaches the base line after a short period of time. In the case of incomplete digestion, 'tailing' would occur and the base line would sometimes not be reached.

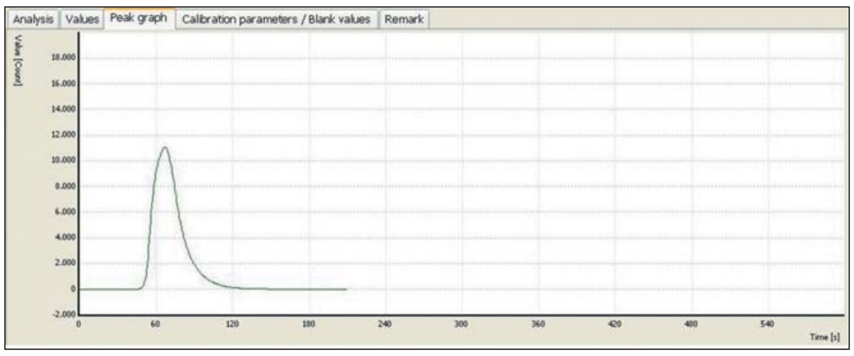

Figure 2. Example of a TS measurement curve with an additive

In the case of TC determination, the ground initial mixture of glass and carbon black was determined. This is a finely ground powder which is able to absorb CO_2 from the air. For this reason, 10% phosphoric acid was previously added to the samples and the standard and this removed at approx. 100°C to dryness. Digestion was carried out without the use of additives in an oxygen stream at 1100°C. The results are summarised in *Table 2*.

Table 2. Results of the TC measurement of different carbon black/glass mixtures

Batch	TC [%]	SD [%]
Sample 1	0.272	± 0.0056
Sample 2	0.275	± 0.0050
Sample 3	0.281	± 0.0021
Sample 4	0.279	± 0.0053

The course of such a TC measurement is shown in *Figure 3*.

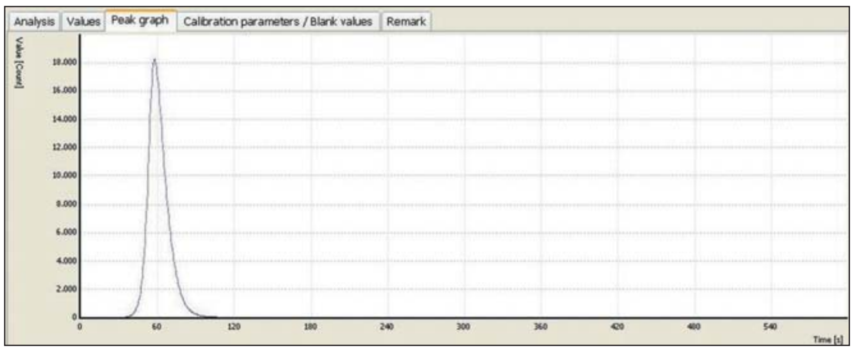

Figure 3. Example of a TC measurement curve

Summary

As it could be shown, the multi EA® 4000 is suitable for determining the TS and TC parameters, even of difficult samples, such as the glasses shown here. In addition to short analysis times, the analyser is characterised by low standard deviations. The two parameters cannot only be determined individually, but also in parallel, in just a single measurement. Furthermore, the analyser has a modular design, which means that the system can be extended to include the element chlorine. In addition, not only the total carbon, but also different carbon parameters can be determined fully automatically. For example, inorganic carbon (TIC), organic carbon (TOC), elemental carbon (EC) or degradable organic carbon (AOC).

Automated Blood Culture Systems Deployed to Afghanistan

The Ministry of Defence has purchased three BacT/ALERT® 3D 60 automated blood culture systems to help deal with combat casualties at the Camp Bastion Field Hospital in Afghanistan. This very sophisticated field hospital, one of the busiest Role 3 NATO hospitals in Afghanistan, provides life saving treatment for wounded military personnel from the British, US and other International Security Assistance Forces (ISAF) in Helmand Province, as well as Afghan national security forces and civilians.

Early in 2011, an Urgent Operational Requirement was identified for automated blood culture analysis capabilities for the rapid diagnosis of bacteraemia and septicaemia in this challenging environment. Dave Scorer, Urgent Operational Requirements Project Manager within the MOD Medical and General Supplies project team (M&GS), explained: "Most contemporary combat injuries in Afghanistan are sustained during dismounted patrols which, like any other field condition, pose a major risk of heavy contamination of wounds and an increased risk of septicaemia. By automating blood culture analysis, we aimed to release BMSs from time-consuming manual techniques, allowing them to give greater attention to trauma situations, for example, with blood transfusions."

He added: "The BacT/ALERT 3D 60 from **bioMérieux** is particularly compact and robust – an especially important consideration in a hot and dusty environment – and is very intuitive and straightforward to use. Two systems are now operational in Camp Bastion, with the third remaining in the UK in the Pathology School in Keogh Barracks, Aldershot, for all operators to be trained before deployment. From start to finish, the lead time from contract award to delivery was three months, with delivery two months ahead of schedule. The feedback has already been excellent; it is making such a difference, saving about half a day of processing."

Circle no. 134

Computerised Particle Analysis for Fine Sample Materials

The Haver CPA 2-1 has been designed by **Haver & Boecker** OHG for particle analysis of dry and non-agglomerating material from 25mm down to 34µm. It meets the expectations of users who need an efficient and at the same time economic particle analyser for their laboratory environment. By using a GigE-camera the CPA 2-1 can also be operated with a notebook, which provides a high degree of mobility and flexibility.

All Haver CPA measuring instruments are based on a digital image processing. A high-resolution digital line scan camera scans the particles in free-falling bulk materials against the background of an LED light source with a recording frequency of up to 28,000 line scans per second. The shadow projections of the particles are evaluated in real time (Haver Real Time function).

Thus the Haver CPA 2-1 can also be utilised as a particle counting device.

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