Application Note · multi EA® 5000

Challenge

Fully automated quantitative digestion of different types of mono- and polysaccharides (sugar and starch) in a wide concentration range, without soot formation and system contamination.

Solution

Time- and matrix-optimized horizontal combustion using flame sensor technique.

Total Nitrogen Determination in Sugar and Starch by Catalyst-Free High-Temperature Combustion and Chemiluminescence Detection

Introduction

Saccharides, often commonly referred to as sugars and starch, are important ingredients in food production, e.g. in soft drinks, confectionery and others. The possibility of easily and quickly converting them into alcohol by fermentation processes also makes them interesting for the chemical industry and for fuel production (e.g. bio ethanol, E10).

Sugars can be produced in many ways, either directly by refining processes from natural sources (sugar cane, beet root) or industrially by enzymatic hydrolysis of starch (corn, potato) with amylase. Depending on the origin and type of raw materials and the production process, the final products can contain different amounts of nitrogen. In raw materials the present TN content results from natural (plant metabolism, minerals) or artificial sources (fertilizers), but it can also be incorporated into the product during the production process. No matter where they come from, N-compounds are undesirable due to the lower quality of the final products (purity, formation of byproducts). But also during the refining of sugar from sugar plants, increased nitrogen content has a negative effect on the ratio between molasses and sugar. That's why determination of the parameter TN is an integral part of process control and quality assurance. Due to the widely varying concentrations, down to trace contents, elemental analysis coupled with highly sensitive chemiluminescence detection has proven to be the best suited technique for this challenging task.

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Oxygen-rich aliphatic or polycondensed cyclic materials such as mono- (dextrose, maltose), oligo- or polysaccharides (starch) tend to decompose thermally when being heated. This severe reaction releases lighter molecules such as water and short-chained hydrocarbons under smoke formation, while the remaining materials form unsaturated pyrolysis products which are condensed even higher. This is a real challenge for analytical technology. A controlled and complete conversion, which is essential for reliable analytical results, becomes impossible.

Flame sensor technology facilitates time and matrix-optimized decomposition. The smart sensor used in the multi EA® 5000 ensures the quantitative combustion of all components without splattering during melting, fuming off, explosive ignition or soot formation. This avoids outliers or TN results that are too low as well as a contamination of the analysis system.

Materials and Methods

3 different sugar and starch samples were analyzed.

Samples and Reagents

- 2 sugar and 1 starch sample
- AJ calibration kits 0–500 mg/l pyridine in isooctane

Sample Preparation

No special sample preparation steps were applied.

Calibration

Prior to the measurements of the samples, the multi EA® 5000 was calibrated for nitrogen determination. Standards based on pyridine in isooctane in a concentration range from 0.1 to 500 mg/l were applied. The calibration was checked with certified reference standards. As an example the calibration curve for the trace range is depicted in Figure 1.

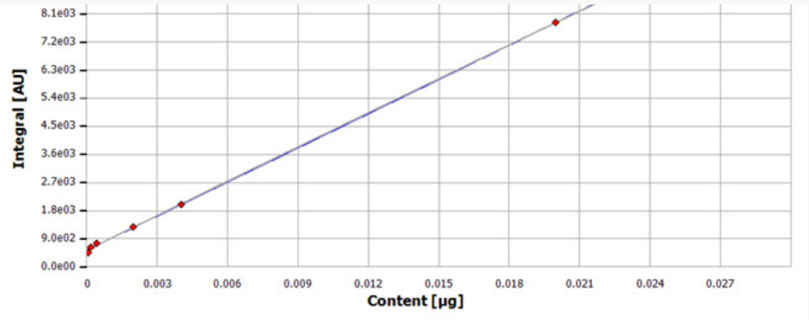

Figure 1: Example TN calibration for the trace range

Instrumentation

A multi EA® 5000 equipped with CLD for the determination of nitrogen was used in horizontal operation mode. For the automated sample introduction and transfer into the analyzer the system was equipped with an automatic boat drive with flame sensor technology and the MMS 5000 multi matrix sampler in solids configuration. To prevent sample contamination resp. loss of the powder shaped samples, the solids autosampler was equipped with a protective cover.

All samples were analyzed in solids mode, sample masses between 5 and 30 mg were applied. For test standards the liquids mode was used with volumes of 20 µl.

The sample digestion was carried out by efficient catalyst-free high-temperature combustion in a quartz tube. This helps to minimize maintenance efforts and costs remarkably. The combustion process is automatically controlled and adopted to the special needs of every matrix component by the flame sensor technology, ensuring optimal matrix-independent results in the shortest possible time. The process is split into two phases. First, evaporation of light components and pyrolysis of the heavier ones takes place within an inert argon atmosphere. The resulting gaseous products are converted in pure oxygen atmosphere of the combustion zone. In the second phase the system switches completely to oxygen and the remaining components are combusted quantitatively.

After sufficient drying of the reaction gases, the formed NOx gas is detected by means of a HiPerSens® CLD. The multi EA® 5000 enables a detection limit of 30 ppb TN. Depending on the sample matrix and type of nitrogen compounds, concentrations as high as 1 wt-% can be determined.

Method Parameters

The 3 given samples were analyzed in solids mode. The process parameters are summarized in Table 1.

Table 1: Process parameters TN determination

Parameter	Specification
Furnace temperature	1050 °C
2nd combustion	60 s
Ar flow (1st phase)	100 ml/min
O_2 main flow	300 ml/min
O_2 flow (2nd phase)	100 ml/min
Purge	35 s

Standard method settings from the method library were applied. The parameter settings for the detection system are summarized in the following table.

Table 2: Process parameters TN determination

Parameter	Specification
Max. integration time	600 s
Start	0.2 ppb
Threshold	0.5 ppb
Stability	7

Evaluation Parameters

The calculation of the TN results was performed automatically by the.

Results and Discussion

Results

The average results of the 3 single analyses together with the calculated RSD values for the given samples and test standard are shown in Table 3. Typical measuring curves are depicted in Figures 2–4.

Table 3: Summarized results of TN measurements of samples and standard

Parameter	TN	
	Result	**RSD**
Dextrose	2.73 mg/kg	**1.85 %**
Maltose	7.73 mg/kg	**3.23 %**
Starch	475 mg/kg	**1.83 %**
TN standard 5 mg/l	5.01 mg/l	**2.16 %**

Due to the matrix-optimized combustion a threefold determination in general is sufficient to reach results around 3 % RSD. This is remarkably affecting the sample processing time and thereby generating a higher sample throughput. The analysis results received and their reproducibility depict the high quality of the digestion process. The proper performance of the analysis system was approved by analyzing a standard material for N determination (see Table 3).

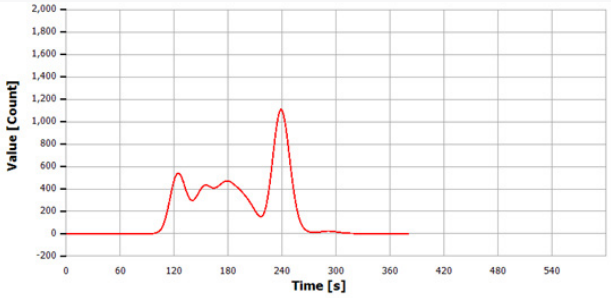

Figure 2: Typical TN measurement curve of dextrose

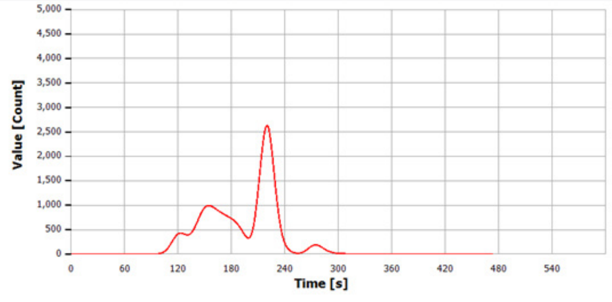

Figure 3: Typical TN measurement curve of maltose

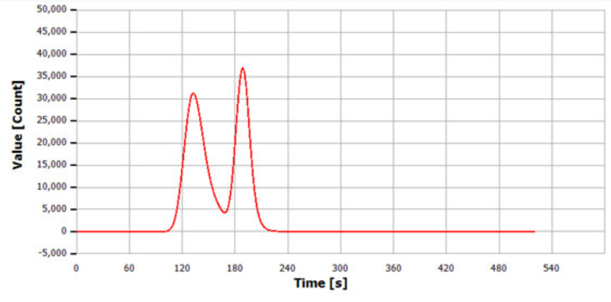

Figure 4: Typical TN measurement curve of starch

Conclusion

The multi EA® 5000 with flame sensor technology facilitates time- and matrix-optimized decomposition, which is crucial for the fast and reliable analysis of challenging matrices such as long-chained, cyclic, condensed and unsaturated samples as in mono and polysaccharides and starch samples. With no effort for development of specific boat programs for each sample a maximum efficiency is ensured by minimum maintenance need.

Thanks to the quantitative combustion a matrix-based calibration of the system with expensive sugar or starch standards is not necessary. Instead, easily available cost-effective isooctane-based pyridine standards can be used. This clearly affects analysis costs and ensures minimum operation effort.

The used HiPerSens® detection system for nitrogen allows analyzing samples in the widest possible concentration range with only one analysis method and without the necessity of additional time-consuming pretreatment. This positively affects the processing time of samples and simplifies the full automation of the analysis process.

Further time-wise optimization can be done by decreasing the sample quantities for highly concentrated sample matrices. The same process and detection parameters can be applied.

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en · 07/2018