Trace Nitrogen Determination in Adipic Acid by Catalyst-Free High-Temperature Combustion and Chemiluminescence Detection

Challenge

Fully automated quantitative digestion of adipic acid to ensure high precision nitrogen results in the trace and ultra-trace range.

Solution

Flame sensor technology for matrix-optimized horizontal combustion combined with HiPerSens chemiluminescence determination for precise N detection down to the sub-nanogram range.

Introduction

Adipic resp. hexanedioic acid is a versatilely used organic compound. Besides its application as a food additive (acidifier), for pH-stabilization in flue gas desulfurization plants, or plasticizer for PVC, the most important application is as a precursor for polymer production. Adipic acid and hexamethylenediamine (hexane-1,6-diamine) are the two monomers used to produce Nylon-66 (Polyamide-66). The polymerization reaction forms an amide link between both monomers by reacting a carboxylic group of the diacid with an amine group of the diamine. Production of high molecular weight Nylon greatly relies on the purity of both monomers. A contamination of adipic acid with amines or other nitrogen-containing compounds is particularly critical because it can lead to termination of the polymerization, unwanted side chains or unspecific building blocks incorporated into the polymer, and thereby impairing product quality.

Nitrogen contamination (TN) in adipic acid may be introduced during its production, which includes oxidation of precursor molecules with nitric acid, and therefore needs to be strictly monitored as a quality parameter. The most sensitive method available today for determination of total nitrogen contents is the combustion-based elemental analysis with TN detection by means of chemiluminescence. Due to its high selectivity and sensitivity even lowest nitrogen quantities in the sub-nanogram range can be detected. But there are still challenges for the analysis technique including contamination from the laboratory

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atmosphere, poor reproducibility, accuracy and precision due to incomplete sample combustion, formation of not detectable nitrogen compounds, and detectability of trace amounts of nitrogen.

The multi EA 5100 with its flame sensor technology facilitates quantitative combustion of all components without splattering during melting, fuming off during pyrolysis, explosive ignition or soot formation. This avoids outliers or TN results that are too low as well as a contamination of the analysis system. This smart sensor ensures not only matrix-optimized digestion, but also a remarkable increase in processing speed and thereby sample throughput while reducing downtime and maintenance to a minimum.

Materials and Methods

Three different adipic acid samples were analyzed. The samples are colorless powders.

Samples and Reagents

- Adipic acid
- Analytik Jena calibration kit 0–25 mg/L N based on pyridine in isooctane

Sample Preparation

Due to the high homogeneity no sample preparation steps were necessary.

Calibration

Prior to the measurements of the samples, the multi EA 5100 was calibrated for nitrogen determination. Standards based on pyridine in isooctane in a concentration range from 0.1 to 25 mg/L N were applied. The calibration has been verified with certified reference standards. 40 µL injections have been applied for the calibration and verification measurements. The different calibration curves are depicted in Figure 1.

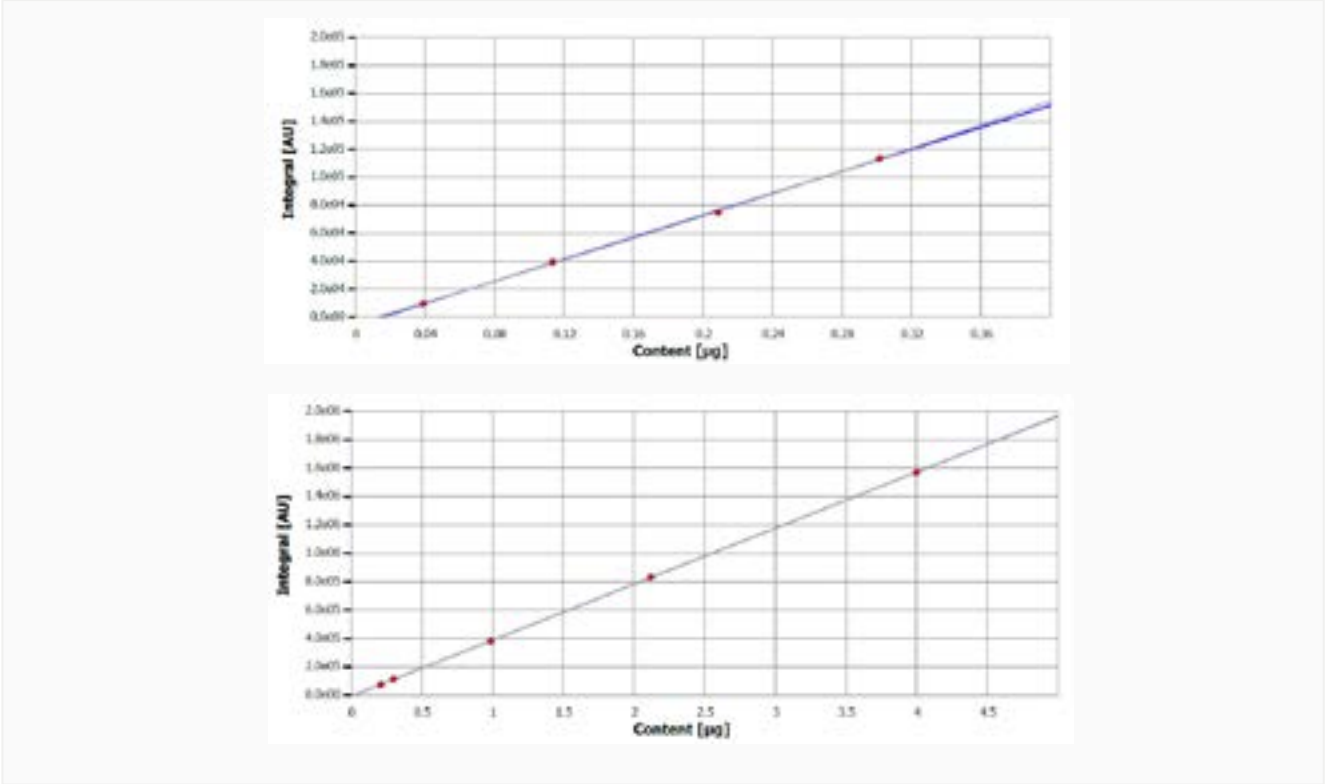

Figure 1: Example calibration curves for the nitrogen determination, trace range (on top) and higher concentration range (below).

Figure 2: multi EA 5100 with MMS in horizontal operation mode

Instrumentation

A multi EA 5100 equipped with HiPerSens 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 Multi Matrix Sampler (MMS) in solids configuration. To prevent sample contamination resp. loss of the powder shaped samples, the solids autosampler can be equipped with a protective cover. All samples were analyzed in solids mode, sample masses between 50 mg and 60 mg were applied. For test standards the liquids mode was used with volumes of 40 µL.

The sample digestion was carried out by efficient catalyst-free high-temperature combustion, at 1050 °C, 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 combusted in pure oxygen. In the second phase the system switches completely to oxygen and the remaining components are converted quantitatively. The implemented Auto-Protection System guarantees highest operational safety (particle and aerosol trap) and a complete transfer (no condensation loss) of the formed gases into the detection unit. There the determination of the nitrogen content is carried out by means of chemiluminescence. The multi EA 5100 enables a detection limit of 10 µg/L N.
The adipic acid samples were analyzed using a library method for solids TN_solid. The calibration and liquid test standards were measured by means of a library method for liquids TN_liquid_H. The process parameters of both are summarized in Tables 1 and 2.

Table 1a: Process parameters of solids method

Parameter	Specification
Furnace temperature	1,050 °C
Second combustion	60 s
Ar flow (first phase)	200 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	200 mL/min
Purge	30 s

Table 1b: Process parameters of liquids method

Parameter	Specification
Furnace temperature	1,050 °C
Second combustion	60 s
Ar flow (first phase)	200 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	200 mL/min
Sample draw up	1 µL/s
Sample injection	3 µL/s
Max. cooling time	240 s

Table 2: Detection parameters of the applied methods

Parameter	Specification
Max. integration time	360 s
Stability	7
Start	1.9 ppb
Threshold	2 ppb

Evaluation Parameters

The calculation of the TN contents was performed automatically by the multiWin software.

Results and Discussion

The results given in Table 3 are averages of three replicate analyses of samples and test standards.

Table 3: Results of nitrogen determination

Sample ID	C_N	SD
Adipic acid 1	2.41 ppm	± 0.01 ppm
Adipic acid 2	2.33 ppm	± 0.07 ppm
Adipic acid 3	1.52 ppm	± 0.11 ppm
CRM (0.98 mg/L)	1.05 mg/L	± 0.02 mg/L
CRM (5.22 mg/L)	5.18 mg/L	± 0.05 mg/L

Due to the matrix-optimized combustion, a threefold determination is generally sufficient to achieve reasonable low RSD values. This is affecting the sample processing time and thereby generating a higher sample throughput. The analysis results and their reproducibility show the high quality of the digestion process. A proper performance of the system was approved by analyzing a reference material for N determination. A representative measuring curve for an adipic acid and a standard is shown in Figure 2and 3.

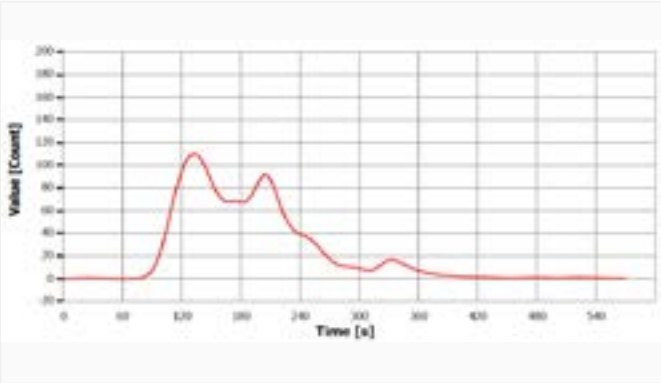

Figure 2: Typical TN measurement curve of adipic acid

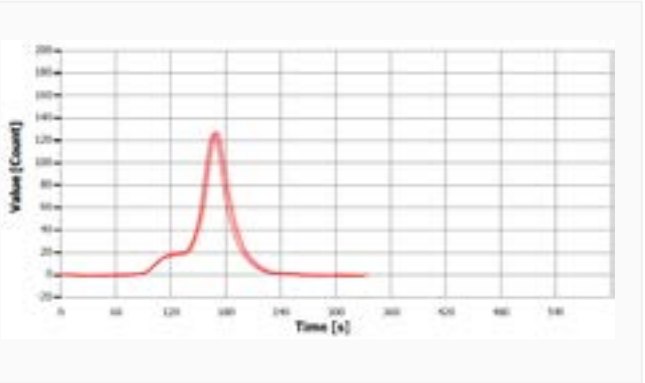

Figure 3: Typical TN measurement curve of N-standard

Conclusion

The multi EA 5100 with flame sensor technology enables time- and matrix-optimized decomposition, which is crucial for the fast and reliable analysis of challenging matrices such as powdered solid adipic acid. Maximum efficiency is guaranteed because no special boat programs have to be developed and maintenance is reduced to a minimum. The HiPerSens detection system for the determination of nitrogen allows analyzing samples in the widest possible concentration range without the necessity for additional time-consuming pretreatment. This further contributes to a fast sample processing time.
Thanks to its modular design the multi EA 5100 can be extended flexibly at any later time. Upgrades to determine other elements like chlorine, sulfur and carbon in other sample matrices, e.g., liquids, gases, and LPG are available.

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