Challenge

Quantitative digestion of lactic acid without soot formation in the shortest measurement time.

Solution

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

Safe and Fast Determination of N/S/Cl Contents in Lactic Acid by Means of Organic Elemental Analysis

Introduction

Lactic acid is one of the most popular biochemicals in the food, animal food and cosmetics industries and a valuable starting material for the production of sustainable biopolymers. Especially in the food industry it is used in many ways, e.g., as an additive to regulate the pH value or to improve the taste of beverages, to extend the shelf life of refrigerated food and dairy products or as antibacterial agent. Lactic acid is a true all-rounder, which has led to a rapid increase in demand. As a result, industrial production is becoming increasingly important.

Lactic acid is mainly produced by fermentation of starch- or sugar-rich biomaterials (e.g., corn, molasses, grass silage, whey, etc.). These natural precursors and the manufacturing process have a direct influence on the sulfur, chlorine and nitrogen concentrations in the lactic acid and lactates. Impurities need to be strictly monitored as they can have undesirable effects on food quality, safety and shelf life. Elemental analysis provides an optimal tool for the reliable determination of those elements by combustion analysis.

Precondition for correct analysis results is a quantitative combustion of all sample types (solid, liquid, highly viscose) independent of their physical properties (boiling/melting point, digestion behavior). The innovative flame sensor technology of the elemental analyzer multi EA® 5000 automatically optimizes the combustion process to the specific needs of any matrix type, quantity and

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composition. This effectively prevents soot formation and contamination of the analyzer and reduces maintenance efforts to a minimum. Furthermore the automated process reduces the need for time-consuming and error-prone development of matrix-specific boat programs, enabling fast and reliable sample analysis.

Materials and Methods

Two different lactic acid samples of two grades (A and B) were analyzed. Lactic acid is a highly viscous colorless liquid.

Samples and Reagents

- Lactic acid
- Analytik Jena calibration kits 0–100 mg/l dibenzo thiophene, pyridine and 2,4,6 trichlorophenol 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, sulfur and chlorine determination. Standards based on pyridine, dibenzo thiophene and 2,4,6-trichlorophenol in isooctane in a concentration range from 0.1 to 100 mg/l were applied. The calibration has been verified with certified reference standards. The different calibration curves are depicted in figures 1 a–3 b.

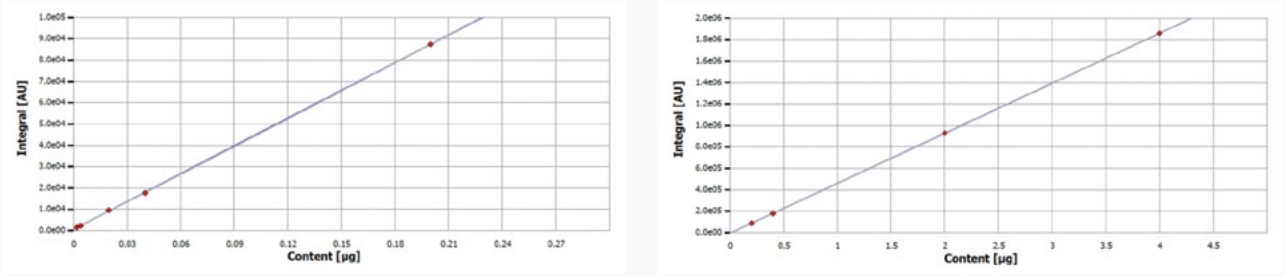

Figure 1 a–b: Multi-range calibration for the parameter TN, trace range (left) and high range (right)

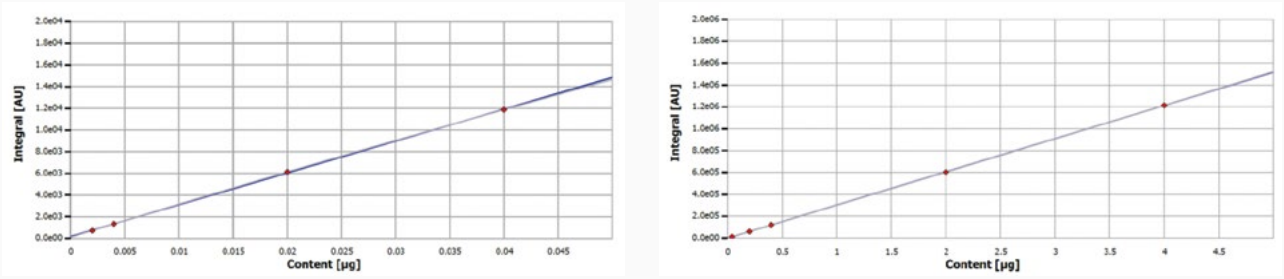

Figure 2 a–b: Multi-range calibration for the parameter TS, trace range (left) and high range (right)

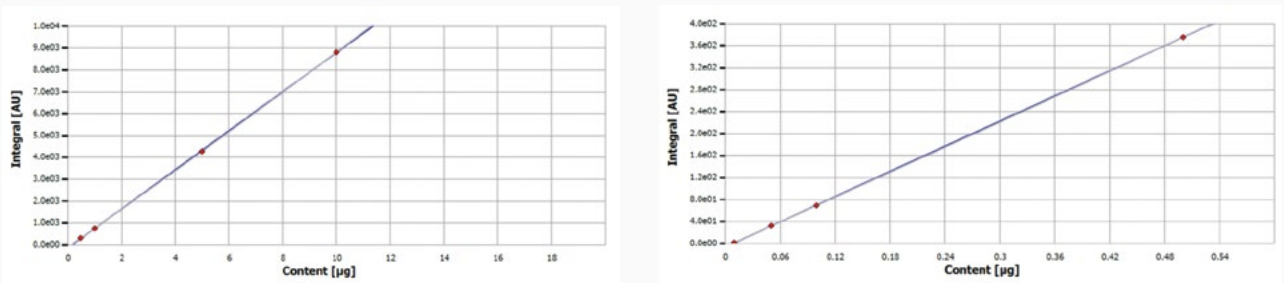

Figure 3 a–b: Multi-range calibration for the parameter TCl, trace range (left) and high range (right)

Instrumentation

A multi EA® 5000 equipped with CLD, UVFD and coulometric detection for the determination of nitrogen, sulfur and chlorine was used in horizontal operation mode. For 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.

The injection volume for lactic acids and test standards were either 20 µl for the TN/TS or 100 µl for the TCl determination. The sample digestion was carried out by efficient catalyst-free high-temperature combustion in a quartz tube. This process is controlled and adapted to the special needs of every matrix component fully automatically thanks to the flame sensor technology. This ensures matrix-independent, optimal results in the shortest possible time. The process is split into two phases. In the first phase the light components are evaporated and the heavier components are pyrolyzed in 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.

The implemented Auto-Protection System guarantees highest operational safety (particle and aerosol trap) and a complete transfer (no condensation loss) of the formed HCl into the "high sensitive" cell. Afterwards the determination of the chlorine content is carried out by means of a micro-coulometric titration. The multi EA® 5000 enables a detection limit of 50 µg/l Cl. Depending on the cell type used, Cl contents up to 10 wt-% can be analyzed directly. SO_2 and NO_x were detected simultaneously with a UV fluorescence resp. chemiluminescence detector.

Method Parameters

Lactic acid samples were analyzed using methods for liquid samples. Due to the high viscosity of the samples the draw up speed of the syringe was set to a minimum. The process parameters are summarized in Table 1 and 2.

Table 1: Process parameters N/S/Cl – liquids method

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
Draw up	1 µl/s
Injection	3 µl/s
Max. cooling time	360 s

Table 2: Process parameters N/S/Cl – solids method

Parameter	Specification
Furnace temperature	1050 °C
2nd combustion	120 s
Ar flow (1st phase)	100 ml/min
O_2 main flow	300 ml/min
O_2 flow (2nd phase)	100 ml/min
Purge	100 s

Standard method settings from the method library were applied. The parameter settings for the different detection systems are summarized in the following tables.

Table 3: Detection parameters N/S

Parameter	Specification N/S
Max. integration time	600 s
Start (N)	0.2 ppb
Threshold (N)	0.5 ppb
Start (S)	0.1 ppb
Threshold (S)	0.11 ppb
Stability	7

Table 4: Detection parameters Cl

Parameter	Specification Cl
Max. integration time	1200 s
Threshold value	300
Max. drift	100
Threshold	25
Cell temperature	23 °C
Titration delay	30 s

Evaluation Parameters

The calculation of the TN, TS and TCl results was performed automatically by the multiWin® software.

Results and Discussion

The average results of the three single analyses together with the calculated RSD values for the samples and three test standards are summarized in Table 5. Typical measuring curves are depicted in Figures 4 a–6 b.

Table 5: Summarized results of TN, TS and TCl measurements of lactic acid and FDCA samples

Standard	TN		TS		TCl	
	Result	RSD [%]	Result	RSD [%]	Result	RSD [%]
Lactic acid grade A*	5.60 mg/kg	**0.84**	3.89 mg/kg	**0.40**	1.01 mg/kg	**1.07**
Lactic acid grade B*	13.30 mg/kg	**0.52**	13.20 mg/kg	**0.29**	21.04 mg/kg	**0.32**
TN standard 10 mg/l	9.99 mg/l	**0.35**	-		-	
TS standard 10 mg/l	-		10.05 mg/l	**0.30**	-	
TCl standard 10 mg/l	-		-		10.08 mg/l	**1.55**

* the density of lactic acid was taken as 1.206 kg/l

Due to the matrix-optimized combustion a threefold determination is generally sufficient to achieve results within 1 % RSD. This is remarkably affecting the sample processing time and thereby generating a higher sample throughput. The analysis results obtained and their reproducibility show the high quality of the digestion process. A proper performance of the system was approved by analyzing standard materials for N/S/Cl determination (see Table 5).

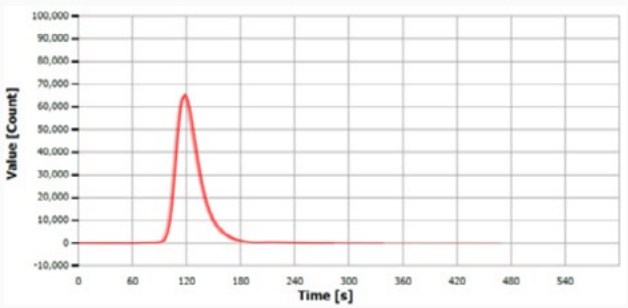

Figure 4 a: Typical TN measurement curves of lactic acid, grade A

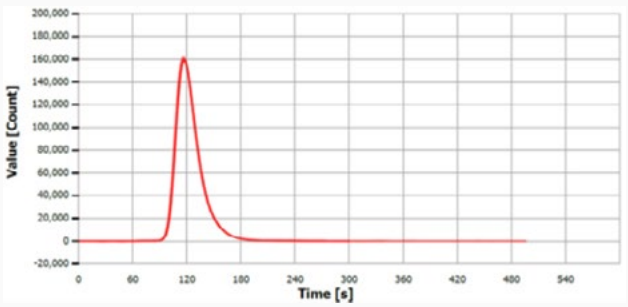

Figure 4 b: Typical TN measurement curves of lactic acid, grade B

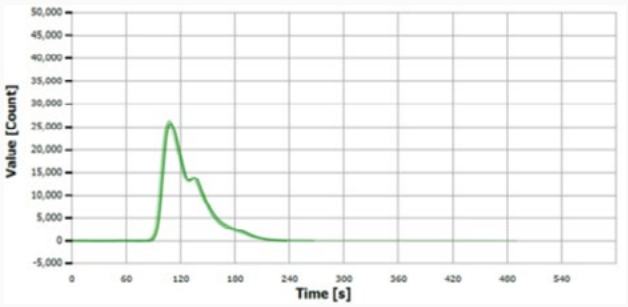

Figure 5 a: Typical TS measurement curves of lactic acid, grade A

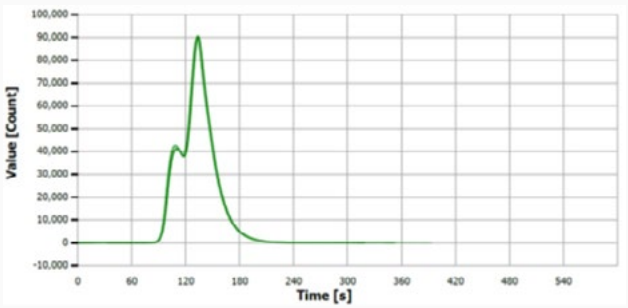

Figure 5 b: Typical TS measurement curves of lactic acid, grade B

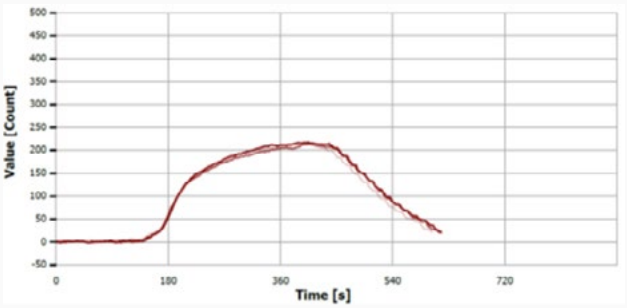

Figure 6 a: Typical TCl measurement curves of lactic acid, grade A

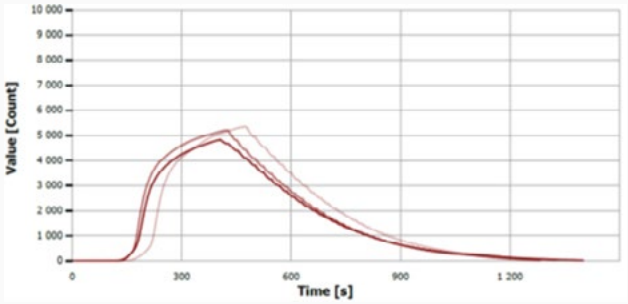

Figure 6 b: Typical TCl measurement curves of lactic acid, grade B

Conclusion

The multi EA® 5000 with flame sensor technology enables time- and matrix-optimized decomposition, which is crucial for the fast and reliable analysis of challenging matrices such as highly viscose lactic acid or solid lactates. Maximum efficiency is guaranteed because no special boot programs have to be developed and maintenance is reduced to a minimum. Further time optimization can be achieved by decreasing the sample quantities for highly concentrated sample matrices. The same process and detection parameters can be applied.

The integrated HiPerSens® detection systems for the determination of nitrogen, sulfur and chlorine allow analyzing samples in the widest possible concentration range without the necessity of additional time-consuming pretreatment. This further contributes to a fast sample processing time.

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