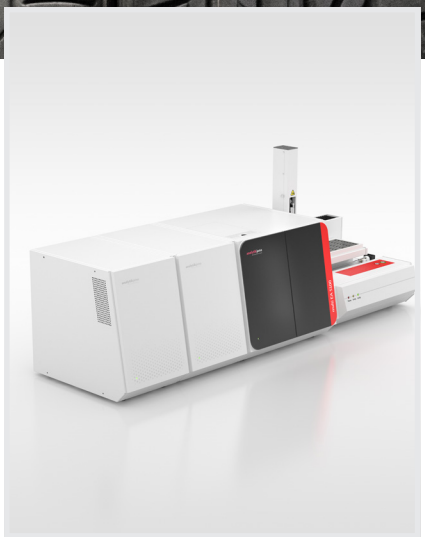

Determination of Total Sulfur and Total Nitrogen in Synthetic Caoutchouc by High-temperature Combustion Coupled with Ultraviolet Fluorescence Detection (UVFD) and Chemiluminiscence Detection (CLD)

Challenge

Fast simultaenous determination of sulfur and nitrogen contents in reactive solid polymer materials. Controlled quantitative soot-free combustion by time-saving direct analysis.

Solution

Horizontal combustion with HiPerSens UVFD resp. CLD combined with flame sensor technology for matrix-independent quality of results.

Introduction

Synthetic caoutchouc is a class of different elastomers (e.g., silicone-, nitrile-, polyether-based, etc.), which are raw materials for the production of rubber (used for production of tyres, sealings, conveyor belts, etc.). Due to its ease of manufacture, the best known representative is styrene-butadiene-rubber (SBR), a copolymer made of 1,3-butadiene and styrene by emulsion polymerization. After polymerization, the SBR is interlaced by vulcanization to change its properties from thermoplastic to elastic. This is done with the aid of sulfur-containing agents and catalysts. The sulfur content of the end product then goes up to the wt% -range. As a measure of quality the parameter sulfur has to be checked for process control and optimization, but also for quality control of the end product. In order to avoid too early interlacing and thus caused unpredictable product quality, structure and properties, the sulfur is also regularly checked for the monomers used as source materials and for the resulting polymerization product. Here the sulfur should only be present in lower quantities.

Due to its suitability for determination of TS contents in a very wide concentration range – from ultra-low contents of 0.2 ng up to several µg of sulfur – the combustion-coupled UV-fluorescence detection has proven to be a valuable tool

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for the daily routine and quality control. It can be utilized for purity checks of the "sulfur-free" starting materials (liquid state), the intermediate SBR, but also for the final interlaced version thereof (solid state).

The multi EA 5100 with flame sensor technology guarantees optimal conditions for any type of matrix, independent of its state of aggregation or digestion behavior. Formation of soot, system contamination, or deflagration caused by a too fast and uncontrolled combustion can easily be avoided. Maintenance and operation effort is reduced to a minimum, which allows to use the system also in shift work or unattended operation.

Materials and Methods

Samples and Reagents

Different rubber samples (styrene-butadiene-rubber) have been analyzed.

- Isooctane (C_8H_{18}), Suprasolv®, GR for gas chromatography (Merck Art.-No.: 1.15440.1000)
- Dibenzothiophene ($C_{12}H_8S$), GR for synthesis (Merck Art.-No.: 8.20409.0025)
- Pyridine (C_5H_5N), GR for analysis (Merck Art.-No.: 1.09728.0100)
- Calibration kits Nitrogen (Analytik Jena, Art.-No.: 402-889.162, 402-889.165)
- Calibration kits Sulfur (Analytik Jena, Art.-No.: 402-889.164, 402-889.167)

Sample Preparation

The given samples were solid materials in the shape of flexible sheets. They were analyzed directly without a pretreatment step (e.g., solution, milling, etc.). This clearly saves time and cost while eliminating a major error source.
For sampling, small aliquots were cut off the sheets using a scalpel. The weight of these aliquots was in the range of 7 mg to 20 mg. Due to the element contents, no higher sample mass was required

Calibration

Liquid calibration standards based on dibenzothiophene (S) and pyridine (N) in isooctane were used to calibrate the analysis system in a wide concentration range. A special calibration with solid materials of the same matrix type (rubber) was not required, due to the matrix-independent quantitative combustion process of the used analysis system.
The calibration was checked with different concentrated standard solutions, the results are given in Table 3 (see page 4).

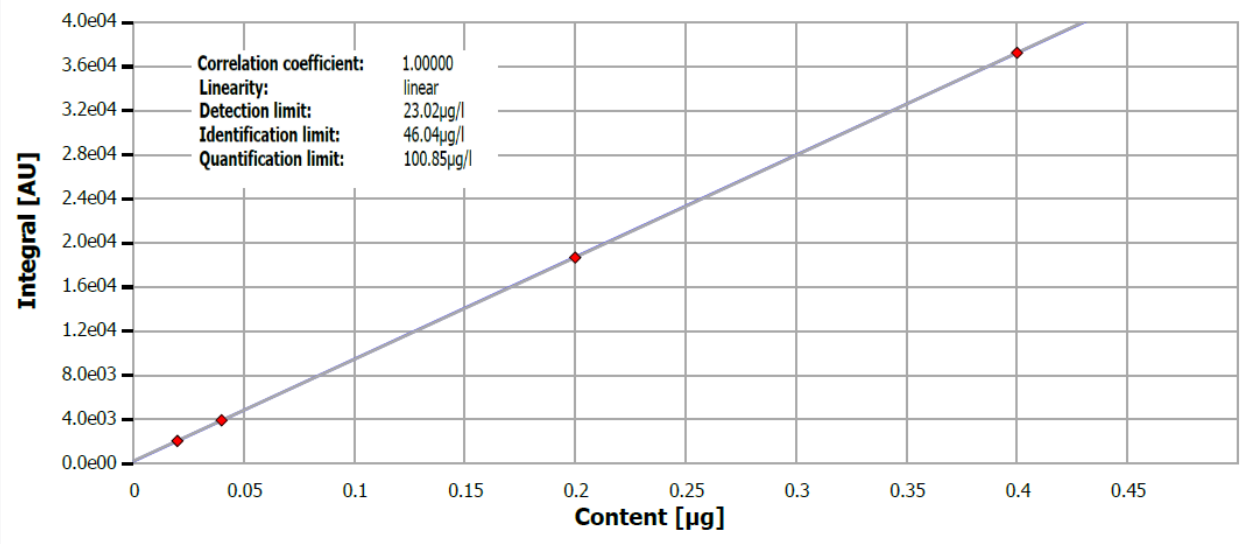


Figure 1: Examplary calibration for TN upper range, curve including statistics

Instrumentation

The measurements were performed using a horizontally configured multi EA 5100, equipped with HiPerSens UV fluorescence and chemiluminiscence detection systems for the determination of sulfur and nitrogen. Sample introduction was carried out fully automatically using the MMS multi matrix sampler in solids mode in combination with the ABD, an automatic boat drive with a cooled sample introduction zone. This ensures a high sample throughput and best analysis results, even for solid samples.

The analyses have been run in horizontal operation mode. Therefore the solid samples were weighed into quartz sample boats, which were placed inside the automatic boat drive by means of the MMS sampling system. Afterwards the ABD fully automatically transfered the loaded boats into the hot zone of the combustion tube. There the catalyst-free, bi-phasic combustion process is carried out at temperatures of up to 1,050 °C. In the first process phase, pyrolysis of the solid sample material takes place in an inert gas stream. This is followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere. In the second phase the resulting solid pyrolysis products as well as the heavier, nonvolatile sample components are quantitatively oxidized in pure oxygen. Thereby the flame sensor technology ensures a uniform evaporation and quantitative combustion for any component of the sample matrix. Incomplete combustion, system contamination and resulting low quality of analysis results is prevented effectively. This establishes the best conditions for analysis of organic solids, even for extremely high sample quantities up to 100 mg. The horizontal mode with flame sensor technology is especially recommended for unknown samples, high element contents, vigorously reacting or any organic solid material (residues, polymers, etc.), but of course it is also suited for any other easy-to-digest samples with lower element contents. The implemented Auto-Protection system guarantees highest operational safety, including a particle and aerosol trap, and a complete transfer of the formed SO_2 into the UVFD resp. NOx into the CLD after a sufficient drying of the reaction gases. The multi EA 5100 enables a detection limit of as low as 5 µg/L S resp. 10 µg/l N.

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

Method Parameters

The methods *TS_UV_hori_solid* and *TS_UV_hori_liquid* from the method library were used for all measurements. The methods are suitable for analysis of liquids resp. solids. Flame sensor technology ensures optimum combustion conditions and effectively prevents soot formation and other incomplete side products which could negatively affect the quality of the analysis for both matrix types. The following table summarizes the parameter settings for the combustion process.

Table 1: Process parameters multi EA 5100 in horizontal mode with flame sensor technology

Parameter	Specification solid mode	Specification liquid mode
Furnace temperature	1,050 °C	1,050 °C
Cooling time (boat)	-	240 s
Second combustion	60 s	60 s
Ar flow (first phase)	200 mL/min	200 mL/min
O_2 main flow	200 mL/min	200 mL/min
O_2 flow (second phase)	200 mL/min	200 mL/min
Draw up	-	2 µL/s
Injection volume	-	40 µL
Injection	-	3 µL/s

Evaluation Parameters

Standard method settings were applied. The parameter settings are summarized in the following table.

Table 2: Detection parameters

Parameter	Specification UVFD	Specification CLD
Max. integration time	600 s	600 s
Start	1.0 ppb	1.9 ppb
Stop	1.1 ppb	2.0 ppb
Stability	7	7

Results and Discussion

The results given in Table 3 are averages of three replicate analyses of samples and test standards. For the samples quantities between 8 mg and 25 mg and for the standards an injection volume of 40 µL were used.

Table 3: Results of the total nitrogen determination in different refinery samples and standards by means of double furnace technology

Measurement	TN	SD	TS	SD
Rubber 1	42.9 mg/kg	± 8.69 mg/kg	359 mg/kg	± 0.12 mg/kg
Rubber 2	38.7 mg/kg	± 0.35 mg/kg	137 mg/kg	± 8.11 mg/kg
Rubber 3	77.8 mg/kg	± 0.51 mg/kg	655 mg/kg	± 6.03 mg/kg
TN Standard (c = 14.5 mg/kg N)	14.7 mg/kg	± 0.28 mg/kg		
TS Standard (c = 435 mg/kg S)			433 mg/kg	± 2.38 mg/kg

Figures 3 – 6 show typical measuring curves for selected samples resp. standards.

Due to the matrix-optimized combustion in general a two- to threefold determination is sufficient for high element contents to achieve reliable results below 3% RSD. This remarkably affects the sample processing time and allows for a higher sample throughput. The analysis results received and their reproducibility prove the performance of the digestion process. The overall performance of the analysis system was validated by analyzing standard materials with known sulfur and nitrogen contents, results are given in Table 3.

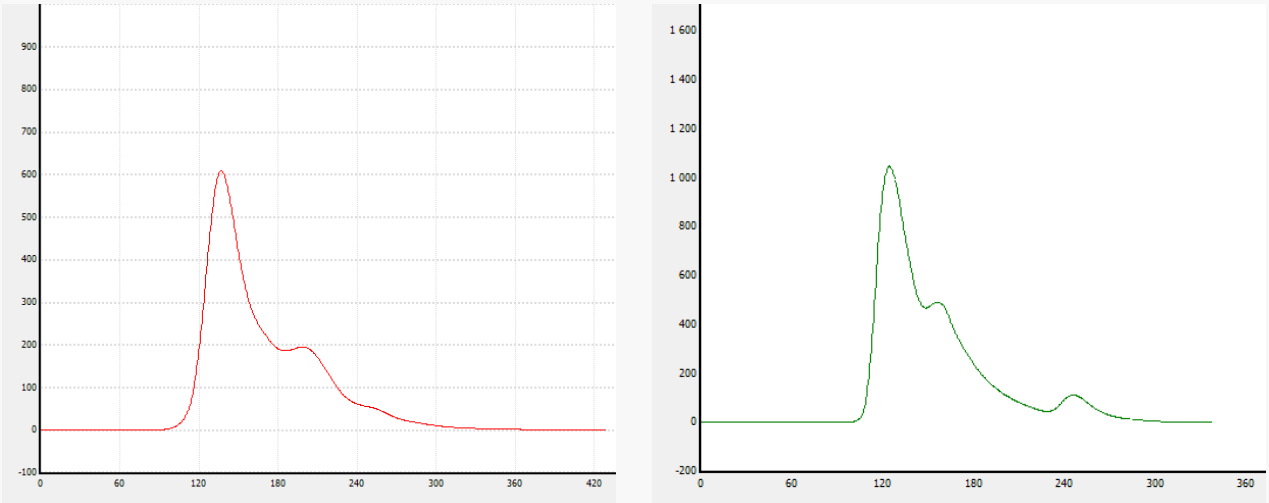
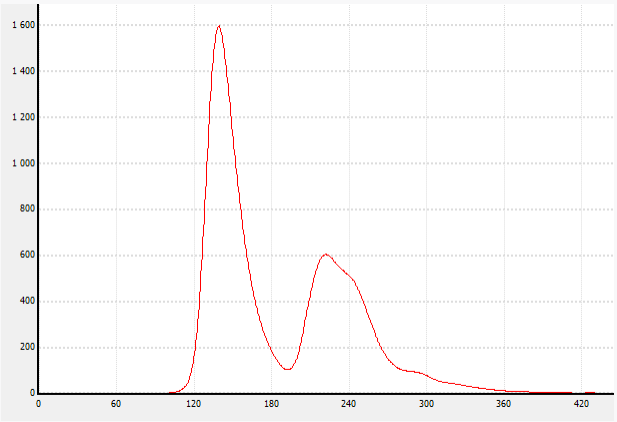


Figure 3a–b: Analysis curves of sample "Rubber 1" – nitrogen (a) and sulfur (b) determination



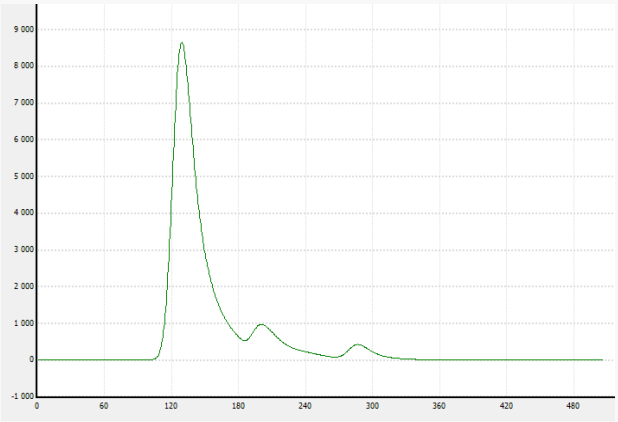


Figure 4a–b: Analysis curves of sample "Rubber 3" – nitrogen (a) and sulfur (b) determination

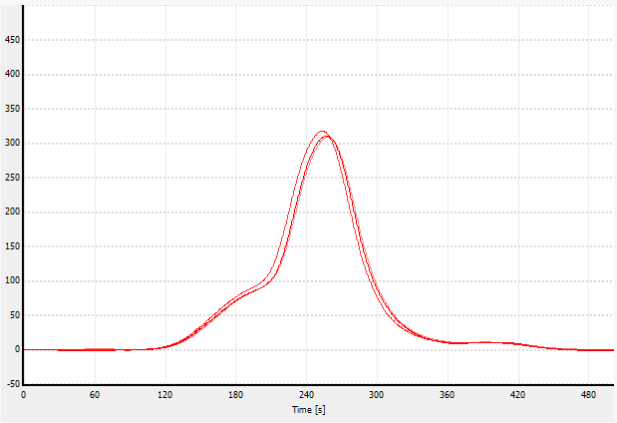


Figure 5: Analysis curve of standard "14.5 mg/kg TN"

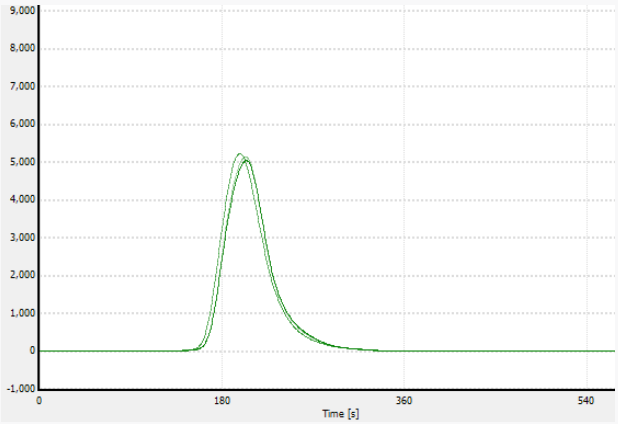


Figure 6: Analysis curve of standard "435 mg/kg TS"

Conclusion

The multi EA 5100 with flame sensor technology provides a fast and reliable solution for the precise simultaneous determination of sulfur and nitrogen contents in solids, even in the most challenging matrices such as polymers. Thanks to the automatically optimized digestion process and the quantitative combustion, best results can be achieved for any matrix, independent of its properties, and in the shortest possible time. This simplifies daily routine work and helps to remarkably increase sample throughput. The fact that the system does not require special matrix-related calibration strategies further reduces the operation and maintenance effort and costs.

Thanks to the unique HiPerSens technology, a measuring range of up to 10,000 mg/L starting at a limit of detection as low as 5 µg/L of sulfur resp. 10 µg/L of nitrogen can be easily achieved. The optimal sample digestion and the efficient Auto-Protection system, including a high capacity membrane dryer, enable excellent reproducibility. A high sample throughput is achieved using the MMS solids sampler. For lower throughput demands manual introduction of the sample boats by means of only the ABD boat inlet system is also possible.

If needed, the analysis system can be extended for the analysis of other matrix types like gases and liquids, or the determination of additional elements and parameters (e.g., chlorine, carbon, TOC, AOX, EOX) by just adding the suitable sampling or detection module.

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Version 1.1 | Author: AnGr
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