Challenge
Time-saving combined determination of organically bound C/N/S/Cl surface contaminations on inorganic materials over a wide concentration range

Solution
Fully automated multi-element analysis in solid samples

Intended audience
Catalyst recycling, catalyst research, catalyst regeneration, catalyst production, quality control labs, refinery labs, contract labs

Combined Determination of Organic Carbon, Sulfur, Nitrogen, and Chlorine Contaminations on Catalyst Surfaces by Combustion Elemental Analysis

Introduction

Catalysts are important auxiliary materials for many refinery processes and processes in the chemical industry, such as hydrogenation, isomerization, dewaxing, or cracking. Very often they consist of crystalline zeolite and noble metals, such as platinum or palladium. During operation, these catalysts can be contaminated by the processed materials. This is also known as catalyst poisoning. The accumulated impurities affect the performance and activity of the catalyst material and stay with the catalyst until it is removed, mainly as surface layers. Especially organic sulfur, nitrogen, and chlorine compounds are hazardous to catalysts. Reaching the threshold for economic performance, the catalyst beds must be replaced. The contaminated material is often regenerated or reactivated by specialized facilities and reused later for the same purpose. The contamination degree of the catalysts is determined for planning of an adequate regeneration, and to check the efficiency of the process. For this purpose, the catalyst material is analyzed for sulfur and nitrogen, but often also carbon and chlorine contents are of interest. While contaminations can vary from upper ppm up to wt-% range, the regenerated catalyst is characterized by rather low contents. To cover this extremely wide concentration range, combustion elemental analysis is perfectly suited with its wide, but still very sensitive, selective detection and the matching combination of all four relevant non-metal elements – nitrogen, sulfur, chlorine, and carbon. The multi EA 5100 belongs to this class of analyzers, combining multi-element analysis with flexible automation possibilities for maximum efficiency of the analytical workflow.

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Materials and Methods

Samples

- 3 solid catalyst samples, spherical shaped pellets and balls

Reagents

- Distilled water, for preparation of carbon calibration solution
- Sucrose (Ph. Eur., VWR Chemicals, Art. No. 27483.294), standard substance for carbon calibration solution
- Calibration kit 10–100 mg/L nitrogen, (Analytik Jena GmbH+Co. KG, 402-889.165)
- Calibration kit 10–100 mg/L sulfur (Analytik Jena GmbH+Co. KG, 402-889.167)
- Isooctane (for gas chromatography ECD and FID, SupraSolv, Merck/Supelco, Art. No. 1.15440.1000), for preparation of Cl test solution
- 2,4,6 trichlorophenol, (for synthesis, Sigma Aldrich, Art. No. 8.18469.0100), standard substance for chlorine test solution

Sample preparation

The given samples were analyzed directly without a pretreatment step.

Calibration

Before analysis, the multi EA 5100 was calibrated. For carbon, nitrogen, and sulfur, liquid calibration solutions were used. The used materials and selected calibration parameters are summarized in Table 1. For determination of high element content, a quicker and simpler way of calibration is to use only one standard. To cover a wide concentration range, the injection volume is varied.

Table 1: Calibration parameters

Parameter	Standard	Concentration range	Element content [absolute]
TC	Sucrose in water	0–1.00 g/L	Up to 50 µg C
TN	Pyridin in isooctane	0–100 mg/L	Up to 5 µg N
TS	Dibenzothiophene in isooctane	0–100 mg/L	Up to 5 µg S

Figures 1 to 3 show example calibration curves for nitrogen, sulfur, and carbon. For the determination of the chlorine content, no calibration was required, since the coulometry is an absolute method and the expected contents are in the lower weight-percent range.

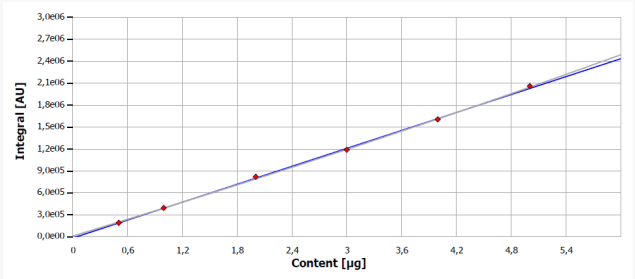

Figure 1: TN calibration curve – middle range

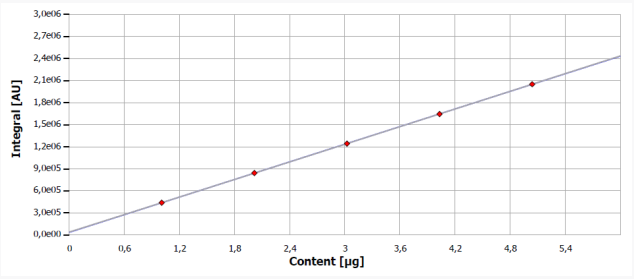

Figure 2: TS calibration curve – middle range

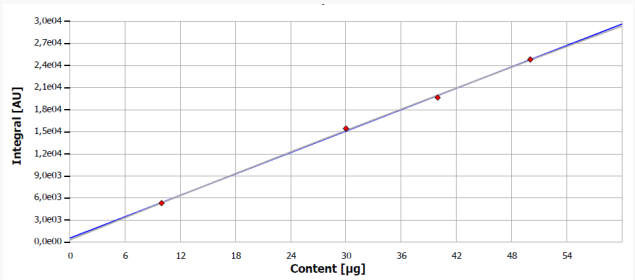

Figure 3: TC calibration curve – middle range

Instrument settings

The analysis has been run on a multi-element analyzer type multi EA 5100 in the horizontal operation mode. The samples were decomposed at 1,050 °C in a two-phase combustion process, which ensures a quantitative combustion of all sample components. For the three solid catalyst materials, the sample introduction was performed automatically by means of the MMS multi matrix sampler in solids mode. Sample quantities were up to three catalyst pellets. For the liquid test solutions and calibration standards the sample injection was performed by MMS in liquids mode automatically. For both checking standards the injected volumes were 40 µL. Sample transfer into the combustion system was done by means of the ABD automatic sample boat drive. The unique flame sensor technology ensures a trouble-free and matrix-optimized combustion of all possible sample types. The detection of the formed NO_x was done by the help of a chemiluminescence detector, the formed SO_2 was detected by the help of a UV fluorescence detector, and detection of CO_2 was done by means of non-dispersive infrared spectrometry. Carbon, nitrogen, and sulfur have been measured simultaneously. The chlorine determination is done sequentially, by aid of coulometric titration. For this purpose, the formed HCl gas is absorbed in the electrolyte solution of the high concentration cell. The integrated Auto-Protection system is switching fully automatically between chlorine and the other three elements, no manual refitting of the analytical hardware is required.

Method parameters

The parameters for combustion and detection are summarized in Table 2 and 3. The injection volume for the liquid standards was 40 µL for C, N, S, and Cl determination. For the catalyst samples quantities in the range of 25 to 45 mg (up to 3 pellets) have been used.

Table 2: Process parameters multi EA 5100 – horizontal mode

Parameter	Settings
Furnace temperature	1,050 °C
2nd combustion	60 s
Ar flow (1st phase)	200 mL/min
O_2 main flow	200 mL/min
O_2 flow (2nd combustion)	200 mL/min
Sample: Draw up***	2.0 µL/s
Sample: Dosing***	2.0 µL/s
ABD mode	automatic*
Purge time**	60 s

* Flame sensor controlled, automatically optimized combustion
** solids mode only
*** liquids mode only

Table 3: Detection parameter for C (NDIR), N (CLD), S (UVFD), und Cl (high concentration cell)

Parameter	Carbon	Sulfur	Nitrogen	Chlorine
Max. integration time	500 s	700 s	700 s	1200 s
Threshold	1.2 ppb	1.1 ppm	2.0 ppb	-
Stability	3	7	7	-
Start	1.0 ppb	1 ppm	1.9 ppb	-
Cell temperature	-	-	-	18 °C
Titration delay	-	-	-	1

Results and Discussion

The results for the simultaneous N, S, C, and the sequential Cl determination of control standards and three different catalyst samples are summarized in Table 4 and 5. They are mean values from three determinations for catalysts and five replicates for the standards.
The samples have been analyzed without further homogenization. Considering the fact that surface contamination of catalyst "pearls" is not perfectly equal for each pearl, the repeatability of the gained results and scatter of replicate analysis is very good. An additional preparation step to generate more homogeneous sample (milling) is possible for further improvement.

Table 4: Results of the N and S determination for the three catalyst samples and control standards

Sample	c_N ± SD	RSD [%]	c_S ± SD	RSD [%]
Catalyst 1	85.1 ± 3.05 ppm	3.59	130 ± 1.82 ppm	1.45
Catalyst 2	128 ± 0.73 ppm	0.94	226 ± 4.82 ppm	2.13
Catalyst 3	34.2 ± 0.61 ppm	1.79	41.4 ± 1.39 ppm	3.36
Standard 145 ppm N	145 ± 2.76 ppm	1.90	-	-
Standard 145 ppm S	-	-	145 ± 0.20 ppm	0.14

The carbon and chlorine contents were determined only for the highly contaminated sample catalyst 3. As test standard for chlorine a 1.45 g/kg Cl solution based on 2,4,6 trichlorophenol was used, for carbon an aqueous sucrose solution with 1 g/L C was applied. The results are shown in Table 5. Figures 4 to 11 exemplarily show C, N, S, and Cl curves for selected samples and control standards.

Table 5: Results of the carbon and chlorine determination of catalyst sample 3 and the control standards

Sample	c_C ± SD	RSD [%]	c_{Cl} ± SD	RSD [%]
Catalyst 3	1.46 ± 0.05 g/kg	0.89	1.15 ± 0.05%	4.68
Standard 1.45% Cl	-	-	1.45 ± 0.03%	1.83
Standard 1.00 g/kg C	1.00 ± 0.03 g/kg	2.72	-	-

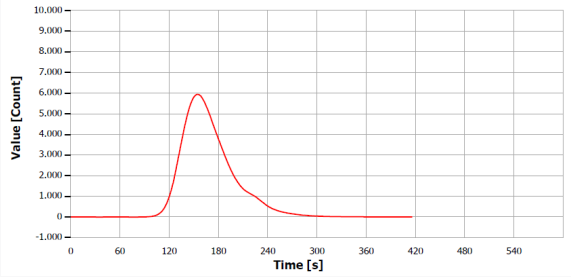

Figure 4: TN measurement curve catalyst 2

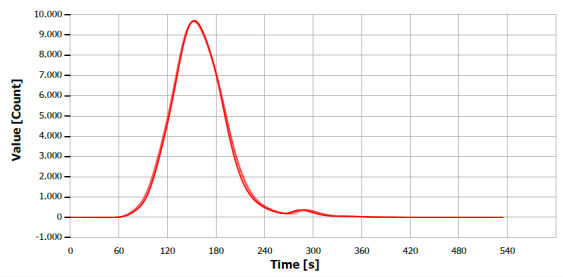

Figure 5: TN measurement curve standard 145 ppm N

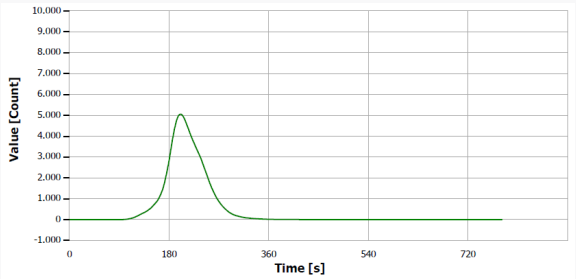

Figure 6: TS measurement curve catalyst 1

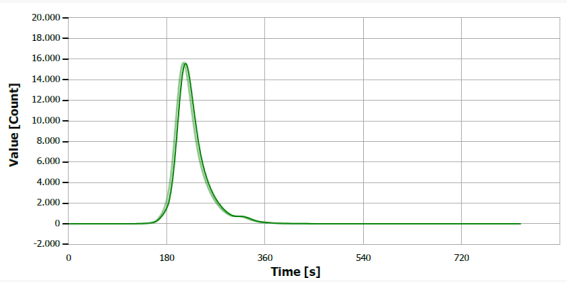

Figure 7: TS measurement curve standard 145 ppm S

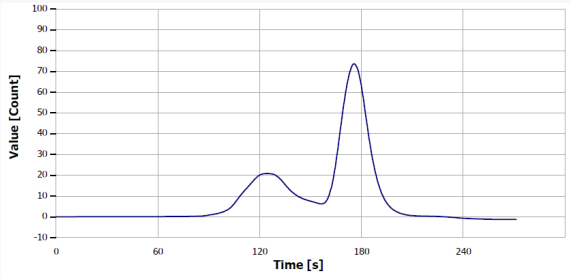

Figure 8: TC measurement curve catalyst 3

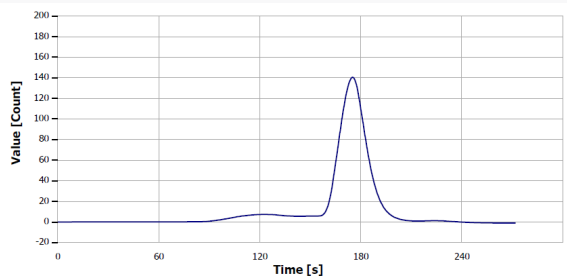

Figure 9: TC measurement curve standard 1.00 g/kg

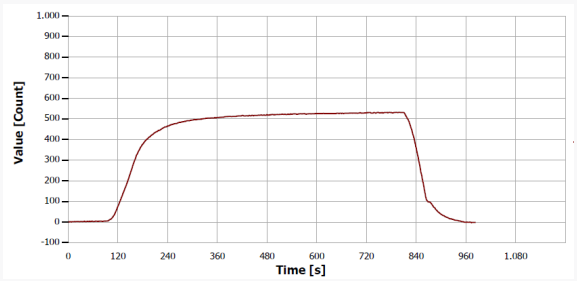

Figure 10: TCl measurement curve catalyst 3

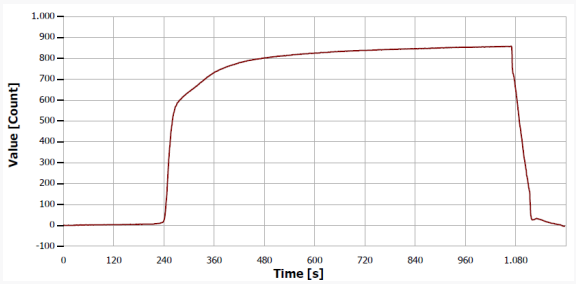

Figure 11: TCl measurement curve standard 1.45 %

Summary

The elemental analyzer multi EA 5100 offers a simple and reliable solution for precise and fast multi-element analysis in solid materials such as catalyst pellets and grains. Sulfur, nitrogen, and carbon contents are determined simultaneously. Chlorine is determined sequentially with the same analyzer without any manual instrument modification. Even very high element contents, which are typical for contaminated catalyst surfaces are, easily analyzed.
Besides analysis of the catalyst material, other process streams, feedstock materials, and final products can also be analyzed with one analysis system. This allows for better comparability between the different matrices, reducing deviations which are commonly caused by utilization of different technology and hardware.
Thanks to the HiPerSens detection C, N, S, and Cl contents in lowest ppb-range can be analyzed too, without adaptations of the used methods. If other analytical tasks come into focus, e.g., analysis of gaseous pyrolysis products, the analyzer can be extended with a gas or LPG sampling system.

Figure 12: multi EA 5100 with ABD and MMS autosampler in solids mode

Recommended device configuration

Table 6: Overview of devices and accessories

Article	Article number	Description
multi EA 5100	450-300.011	Basic module with combustion
C/N/S High Performance drier kit multi EA 5100	450-300.012	High performance reaction gas drier
N module	450-300.022	chemoluminescence detector for nitrogen
S module basic	450-300.021	UV fluorescence detector for sulfur with MPO technology
C module	450-300.028	NDIR detector for carbon
Cl module	450-300.023	Module for determination of chlorine contents by coulometric titration
Extension kit Cl "high concentration"	450-300.026	Extension for determination of very high chlorine contents
Automatic Boat Drive - ABD	450-300.013	Automatic boat drive with flame sensor technology – sample supply in horizontal mode
Multi Matrix Sampler - MMS	450-300.030	Sampler for automatic dosing of liquids, solids, AOX, EOX and TOC samples
Solids kit for MMS 5100	450-300.034	Accessory for the dosing of solid samples
Liquids kit for MMS 5100	450-300.033	Accessory for the dosing of liquid samples
multiWin software	450-011.803	Control and data evaluation software

The configuration described above can also be used to analyze liquid samples such as hydrocarbons, VGO, HCR feed, and fuels that are feedstocks, intermediates, and products of hydrotreating and hydrocracking processes, for which such catalyst materials are used for. Even gaseous compounds could easily be analyzed by just adding one of the optional accessory modules for sample introduction of gas or LPG samples.

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