



Challenge

Automated reliable determination of TC, TN, TS, and TCI contents in viscous, vigorously reacting pyrolysis oils and products of further processing in a wide concentration range

Solution

Combustion based elemental analysis with flame sensor optimized combustion and wide range detection with multi EA 5100 multi element analyzer

Intended audience

Operators of pyrolysis plants, actors in the field of chemical recycling, further processors of pyrolysis oil, operators of refineries, contract labs

Chemical Recycling of Plastics – Analysis of Chlorine, Sulfur, Nitrogen, and Carbon in Pyrolysis Oils, Waxes, and Secondary Products

Introduction

Plastic waste is one of the major problems of our time. The global amount of plastic waste is expected to triple by 2060. Currently, only 9% of it is recycled. The rest is landfilled, burnt with CO₂ emissions, or ends up in the environment, especially in the sea, where it causes severe ecological damage. At the same time, fossil resources, from which plastics have mainly been made so far, are becoming scarcer and less attractive for reasons of climate protection. That is why plastic recycling is becoming more and more important. Only certain plastics are suitable for mechanical recycling, which has been predominant up to now, and they must be well sorted by type, which is why mechanical recycling alone cannot sufficiently increase the recycling rate.

Chemical recycling offers a solution, as it can also use mixed plastic waste. In the pyrolysis process, the polymer chains of mixed plastic waste, especially polyolefins such as PE and PP, are broken down at temperatures around 600 °C in the absence of oxygen. A viscous, brown pyrolysis oil is produced,

which consists of a spectrum of hydrocarbon chains of different lengths and can be reused for plastics production or as fuel. Since monomers such as ethene, propene, and butene are needed to produce new plastics, the hydrocarbon chains of the pyrolysis oil have to be broken down even further. Depending on how heavy or light the pyrolysis oil is, this is done in a refinery and/or in a steam cracker. To avoid corrosion, catalyst poisoning, and other problems, the raw material fed into the petrochemical plants must not exceed certain limits for heteroatoms and metals.

Chlorine, which comes from the polymers itself (e.g., PVC), from additives or dyes, can lead to corrosion by HCl gases in the treatment process. Sulfur, which mainly comes from car tires and other rubber products, can also lead to corrosion, catalyst poisoning, and other problems in the steam cracker. Nitrogen, which comes from polymers like ABS, NBR, or PA, or from additives and impurities, can also lead to catalyst poisoning, fouling in further processing, and formation

of ammonia and cyanides. When being used as fuel, the pyrolysis oil must also comply with stringent legal limits for sulfur emission.

If the pyrolysis oil exceeds the specified element concentrations, mitigation actions are required. To ensure compliance with the specifications and, if necessary, to enable appropriate mitigation actions, a reliable analysis of the total chlorine, sulfur, and nitrogen contents is necessary. Sometimes the carbon content is determined additionally for evaluation of the pyrolysis step. This allows for a correct mass balance.

While other techniques such as X-ray fluorescence analysis (XRF) or combustion ion chromatography (CIC) already reach their limits in covering the relevant elemental combination, combustion based elemental analysis, a technique established for the measurement of non-metal elements in

the field of refinery analysis, allows for the determination of all four elements with a single instrument.

For such a challenging analysis task, the multi EA 5100 – a multi-element analyzer – is perfectly suited. Due to intelligent valve technique and the modular design all relevant parameters can be measured in one analysis cycle. Carbon, nitrogen and sulfur are determined simultaneously. The chlorine content is measured sequentially, fully automatically, without manual system reconfiguration. In some cases, the processed products of the pyrolysis oil are also of interest, namely when high-quality and high-purity chemical specialities (e.g., white oil, wax, solvents) are produced. Thanks to its wide linear measuring range and low detection limits, the multi EA 5100 allows an extension of the analysis for these sample types as well.

Materials and Methods

Samples

Pyrolysis products

- Sample A1 (dark brown, liquid, strong odor, homogeneous)
- Sample A2 (dark brown, liquid, strong odor, inhomogeneous, particle containing)
- Sample B1 (dark brown, liquid)
- Sample B2 (light brown, wax)

Derived products

- Samples C1, C2, C3 (brown, waxes, process intermediates)
- Samples C4, C5, C6 (yellow, oils) white oil
- Samples C7, C8, C9 (white, waxes) paraffin wax
- Sample C10 (clear, colorless, liquid) aliphatic solvent

Reagents

- Isooctane (for gas chromatography ECD and FID, SupraSolv, Merck/Supelco, Art. No. 1.15440.1000), standard substance for carbon calibration, c: 580.41 g/L C
- o-xylene 99% (Thermo Fisher Scientific/Alpha Aesar, Art. No. A11358.AP), solvent for dilutions
- Calibration kit 0.10-25 mg/L nitrogen, (Analytik Jena GmbH+Co. KG, 402-889.075)
- Calibration kit 0.1-10 mg/L chlorine (Analytik Jena GmbH+Co. KG, 402-889.071)
- Calibration kit 0.1-10 mg/L sulfur (Analytik Jena GmbH+Co. KG, 402-889.070)
- Calibration kit 10-100 mg/L chlorine, (Analytik Jena GmbH+Co. KG, 402-889.166)
- 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)

Sample preparation

For N, S, and Cl determination, sample types A and B were homogenized by sample dilution prior to analysis, due to the expected high concentrations, increased viscosity, and partial inhomogeneity. For this purpose, the waxy and inhomogeneous oil samples were homogenized by melting at 60 °C in a water bath first. Then an aliquot of these homogeneous samples was diluted mass-based (m/m) with o-xylene as a solvent. The dilution factors used ranged from 3 to 100, depending on the sample. The blank value of the diluent was determined and taken into account for correction of the final results. The same solvent was used for the homogeneous oil samples, except that the warming-up step was omitted. This strategy allows a fast processing of all samples together with one liquid sampler. Alternatively, a temperature-controlled autosampler can also be used.

Calibration

Before analysis, the multi EA 5100 was calibrated. For this purpose, calibration solutions, in the concentration range from 0 to 100 mg/L, were used for the elements nitrogen, sulfur, and chlorine. For the carbon calibration, a suitable organic liquid, in this case isooctane, can be utilized. The used materials and selected calibration parameters are summarized in Table 1. An injection volume of 40 µL was used for the N, S calibrations and 100 µL for the Cl calibration. Carbon calibration was performed using only one standard, as usual, for the determination of very high elemental contents. To vary the element contents, different volumes of the standard were dosed here. Figures 1 to 4 show examples of the calibration curves.

Table 1: Calibration parameters

Parameter	Standard	Concentration range	Element content (absolute)
TC	Isooctane	580.41 g/L	5.8–29 $\mu\text{g C}$
TN	Pyridin in isooctane	0.1–100 mg/L	0.004–4 $\mu\text{g N}$
TS	Dibenzothiophene in isooctane	0.1–100 mg/L	0.004–4 $\mu\text{g S}$
TCl	2,4,6-trichlorphenol in isooctane	0.1–100 mg/L	0.01–1 $\mu\text{g Cl}$

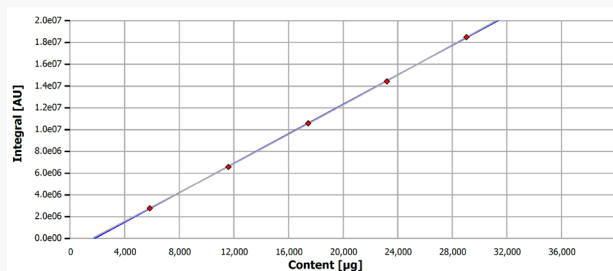


Figure 1: TC calibration curve

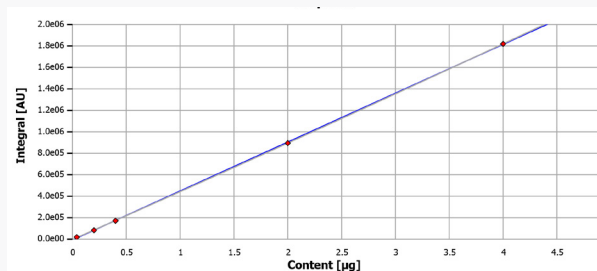


Figure 2: TN calibration curve

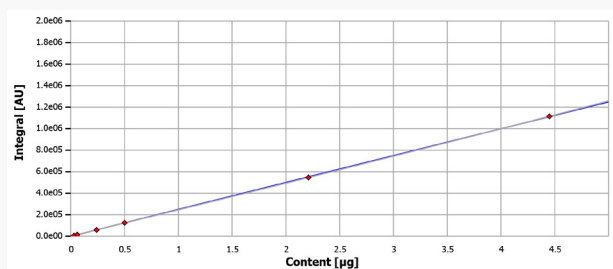


Figure 3: TS calibration curve

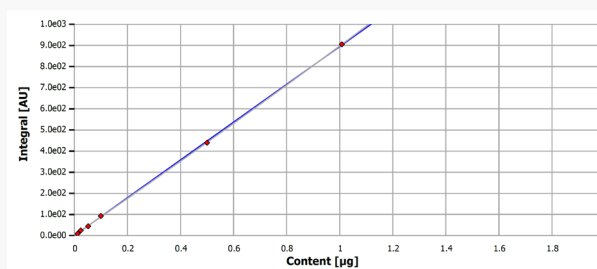


Figure 4: TCl calibration curve

Materials and Methods

Instrumentation

A multi EA 5100 multi-element analyzer was used in horizontal operation mode for the analysis of all samples and standards. A UV-fluorescence detector (UVFD) with MPO technology (micro plasma optimization) was used for the determination of sulfur. MPO is a patented technology preventing interferences caused by high nitrogen concentrations during the determination of sulfur traces and thus false, too high measured results. A non-dispersive IR detector (NDIR) was used for the determination of carbon, a chemiluminescence detector (CLD) was applied for the determination of nitrogen. For the determination of chlorine, coulometric titration using the high sensitivity cell option was used. The achievable detection limits of

the measuring system used are 50 $\mu\text{g/L Cl}$, 5 $\mu\text{g/L S}$, and 10 $\mu\text{g/L N}$.

For automated sample introduction and transfer into the combustion furnace, the system was equipped with an automatic boat drive with flame sensor and a multi-matrix sampler (MMS). The flame sensor ensures safe and quantitative combustion of each sample matrix within the shortest possible measurement time. This eliminates the need for time-consuming method development and creation of boat programs for each sample type. This makes analysis simple and reproducible, eliminates sources of error, and reduces maintenance compared to classic boat programs.

For the measurements, a defined sample volume was dosed into a quartz sample boat, placed in the automatic boat drive (ABD), using the μL -syringe of the MMS. Afterwards this boat is automatically transferred to the combustion furnace, controlled by the flame sensor. The flame sensor adapts the process to the special requirements of the respective sample component, ensuring matrix-independent results. Sample digestion was carried out by efficient catalyst-free high-temperature combustion. The process is divided into two phases. In the first phase, the volatile sample components are vaporized in an inert gas stream, followed by combustion of the gaseous products formed in an

oxygen-rich atmosphere. In the second phase, the heavier, non-volatile sample components and the pyrolysis products formed are quantitatively oxidized in pure oxygen. The formed gaseous reaction products SO_2 , NO_x , CO_2 , and HX are transferred to the respective detection systems after complete drying. The Auto-protection system guarantees highest operational safety and efficient protection. Particles and aerosols are retained, only the analytes can pass. Switching between C/N/S analysis branch and coulometric chlorine detector is done quickly and fully automatically without manual conversion.

Method parameters

A multi-element method from the method library was used for the analysis of the standards and samples. The parameters for combustion and detection are summarized in Tables 2 and 3. The injection volume for the C, N, and S determination was 40 μL . For the chlorine determination it was 100 μL .

Table 2: Process parameters multi EA 5100 – horizontal mode

Parameter	Setting
Furnace temperature	1050 °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 $\mu\text{L}/\text{s}$
Sample: inject	2.0 $\mu\text{L}/\text{s}$
ABD mode	automatic*

* Flame sensor controlled, automatically optimized combustion

Table 3: Detection parameters for C (NDIR), N (CLD), S (UVFD), and Cl (high sensitive cell) detection

Parameter	Carbon	Sulfur	Nitrogen	Chlorine
Max. integration time	500 s	700 s	700 s	1200 s
Stability	7	7	7	-
Start	0.12 ppb	0.2 ppm	0.5 ppb	-
Threshold	0.20 ppb	0.2 ppm	0.5 ppb	-
Cell temperature	-	-	-	22 °C
Titration delay	-	-	-	1
Threshold	-	-	-	300 cts
Threshold value	-	-	-	25 cts
Baseline / drift correction	-	-	-	automatic

Results and Discussion

The results for the simultaneous N, S, Cl determinations of the control standards and different sample types are summarized in Table 4. These are mean values from triplicate determinations. The high efficiency of combustion and sample introduction are reflected in the excellent reproducibility and low scatter of the measurement results, below 3%.

Table 4: Results of the analyses of TN, TS, and TCI for samples and standards

Sample	c _N [mg/L]	RSD [%]	c _S [mg/L]	RSD [%]	c _{Cl} [mg/L]	RSD [%]
C1	64.9	0.59	15.8	0.72	6.7	0.74
C2	78.6	0.35	17.9	1.48	34.2	1.17
C3	59.5	0.75	16.6	2.01	45.2	0.01
C4	83.2	0.12	22.6	1.39	12.5	0.52
C5	63.7	0.27	38.7	2.18	73.7	1.49
C6	50.5	0.39	39.6	0.90	930	0.37
C7	0.46	1.76	0.26	2.99	0.37	2.21
C8	0.46	5.54	0.24	3.86	0.85	3.70
C9	73.0	3.21	0.85	0.21	0.51	2.54
C10	5.70	0.30	35.1	1.13	0.75	0.93
Pyrolysis oils and waxes						
B1	3,250	0.6	2500	0.8	498	2.4
B2	1,410	1.0	78.6*	1.8	84.1	0.4
A1	1,050	0.6	33.9*	1.6	36.4	1.2
A2	1,540	0.01	37.1*	2.5	28.6	3.4
Test standards						
Standard 12.5 mg/L S			12.5	2.45		
Standard 10.1 mg/L N	10.2	0.60				
Standard 10.0 mg/L Cl					9.99	1.24

* TS with MPO

As expected for pyrolysis products, like sample types A and B, the contained sulfur, nitrogen, and chlorine contents are very high. By taking suitable measures, these are noticeably reduced to trace levels before and during further processing, which is clearly shown by the measured values of the samples of type C, in particular C7 and C8.

For samples B1, B2, A2, and A2, the MPO feature was used for the TS measurement in order to avoid interferences caused by the much higher TN concentrations (> 1 g/L TN at TS concentrations in the mg/L range). For UV-fluorescence, NO molecules can cause cross sensitivity, about 1% of the nitrogen concentration is detected false positive as sulfur. In contrast, for samples C1 to C10, where the TN and TS values were in a similar concentration range, MPO is not needed. To show the effect of the MPO on the measurement results, samples A1 and A2 were measured both with and without the use of MPO. The results are summarized in Table 5.

Table 5: Comparison of TS results for samples A1 and A2 – with and without interference correction

Mode	UVFD		UVFD with MPO		
	Sample	c_s [mg/L]	RSD [%]	c_s [mg/L]	RSD [%]
A1		43.1	0.5	33.9	1.6
A2		54.9	1.6	37.1	2.5

The carbon content was determined only for the pyrolysis oils A1 and A2. For this purpose, the samples were measured undiluted. The results are shown in Table 6.

Table 6: Results of TC determination for pyrolysis oils

Sample	c_c [g/l]	RSD [%]
A1	666	0.4
A2	666	0.5
Isooctane, 580.41 g/L C	580.41	0.4

The figures 5 to 18 show representative N, S, and Cl curves for the control standards and for one sample from each of the three different sample groups (C3, B2, A1); a carbon curve for sample A1 and isooctane is also included.

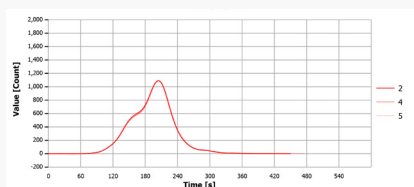


Figure 5: Measurement curve for TN standard 10.1 mg/L

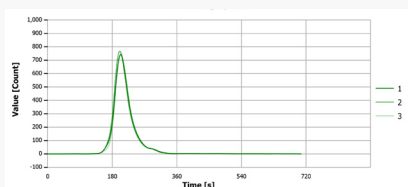


Figure 6: Measurement curve for TS standard 12.5 mg/L

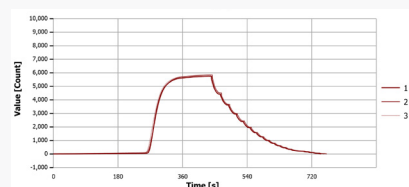


Figure 7: Measurement curve for TCl standard 10 mg/L

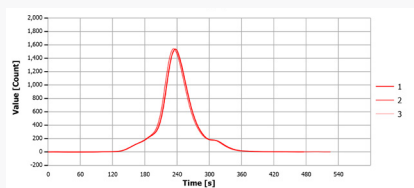


Figure 8: TN measurement curve sample C3

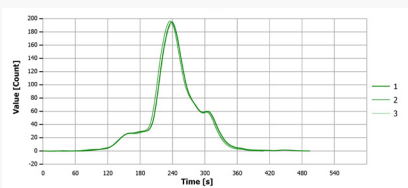


Figure 9: TS measurement curve sample C3

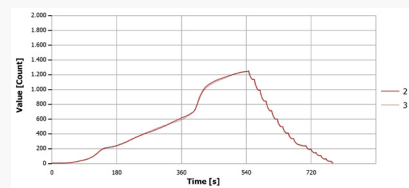


Figure 10: TCl measurement curve sample C3

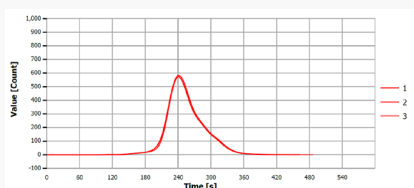


Figure 11: TN measurement curve sample B2

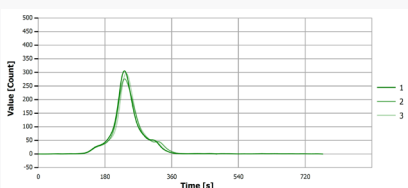


Figure 12: TS measurement curve sample B2

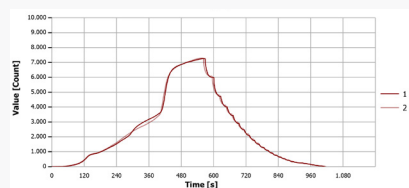


Figure 13: TCl measurement curve sample B2

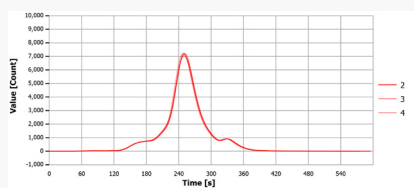


Figure 14: TN measurement curve sample B2

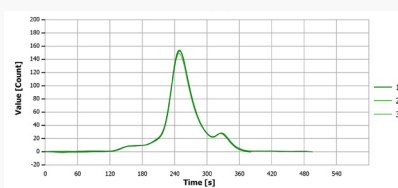


Figure 15: S measurement curve sample A1

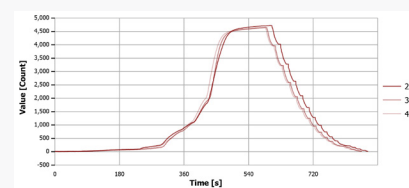


Figure 16: TCl measurement curve sample A1

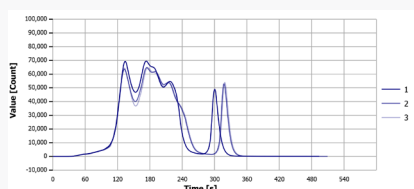


Figure 17: TC measurement curve sample A1

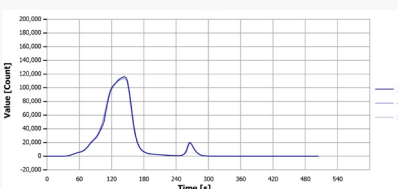


Figure 18: TC measurement curve isooctane

The shape of the measurement curves for the carbon determination appears visually widely varying. This reflects the control behavior of the flame sensor to create optimum combustion conditions. When looking at the analysis results, however, the high reproducibility with less than 1% RSD as an indicator for high repeatability and reliable results becomes apparent.

Summary

The elemental analyzer multi EA 5100 offers a simple and reliable solution for precise and fast multi-element analysis in pyrolysis oils, waxes and products of further processing. Sulfur, nitrogen, and carbon contents are determined simultaneously. Chlorine is determined sequentially with the same analyzer, without any manual instrument modification. The HiPerSens detection provides lowest detection limits and a very wide linear measuring range for C, N, S, and Cl. This allows for the analysis of significantly contaminated pyrolysis oils, process intermediates, and the resulting high-purity end products with the same instrument and analysis method. This saves additional time.

The flame sensor enables reliable, reproducible, and fast digestion of any sample matrix without method development, thus guaranteeing exact results in the shortest possible measuring time. The formation of soot or other undesirable pyrolysis products, the resulting increased maintenance effort, and incorrect analysis results are, thus, prevented from the outset.

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.

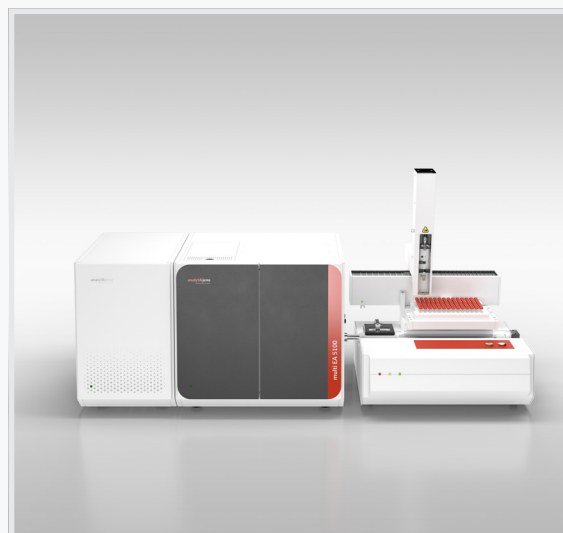


Figure 19: multi EA 5100 with ABD and MMS autosampler in liquids mode

Recommended device configuration

Table 7: Overview of devices and accessories

Article	Article number	Description
multi EA 5100	450-300.011	Basic module with combustion furnace
C/N/S High Performance drier kit multi EA 5100	450-300.012	High performance reaction gas dryer
N module 5100	450-300.022	Chemoluminescence detector for nitrogen
S module MPO 5100	450-300.020	UV fluorescence detector for sulfur with MPO technology
C module 5100	450-300.028	NDIR detector for carbon
Cl module 5100	450-300.023	Module for determination of chlorine contents by coulometric titration
Extension kit Cl "high sensitive"	450-300.024	Extension for chlorine determination in the trace range
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
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 solid samples such as charcoal, which is produced too during pyrolysis.

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Version 1.0 · Author: XY
en · 11/2023

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