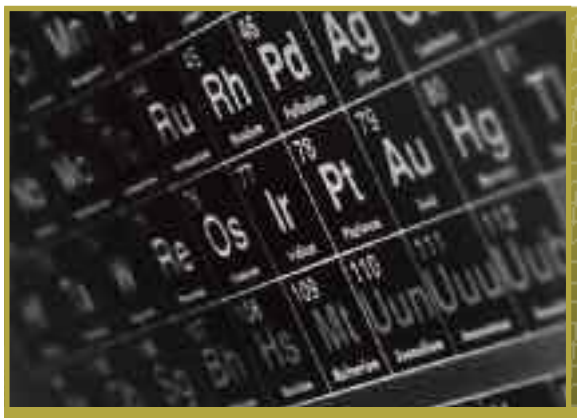

Unlimited Possibilities with the new Multi-Element Analyser multi EA® 5000: Determination of sum Parameters and Element Contents from PPB to Mass Percent

Dr. Angela Gröbel, Product Specialist, Analytik Jena AG, Konrad-Zuse-Str. 1, 07745 Jena, Germany
Phone: +49 (0) 3641 77-70 Fax: +49 (0) 3641 77-92 79 Web: www.analytik-jena.de

The precise, fast and user-friendly determination of quality determining elements, such as sulfur, nitrogen, chlorine and carbon but also the analysis of environmentally relevant sum parameters, is continually gaining significance in modern analysis laboratories in the chemical, petrochemical and many other industry branches. The analysis system multi EA® 5000 is able to determine the contents of the elements sulfur, nitrogen, carbon and chlorine in a single sample cycle. With only one instrument, a broad spectrum of extremely different sample matrices can be analysed for element contents in the range of ultratraces up to mass percent. Conventional measurement tasks from the environmental analysis are also easily mastered with this multi-element analyser.

Introduction

In the petrochemical and other branches of the chemical industry, such as in the manufacture of polymers, many production processes are controlled based on the analysis of existing end products. Also, the addition of catalysts and additives and based on this, the later performance characteristics of the end products, can be precisely controlled in that way. Mainly methods of elemental analysis are used in these cases. The most often determined are the contents of carbon, sulfur, nitrogen or chlorine. With this the expected concentration values can vary from a few ppb (e.g. biodiesel etc.), as a component of contamination, up to the top mass percent range, as main components of the end products (e.g. polymers). However, normally not only one of these elements is significant. Since with commercial manufacturing methods every minute counts, a time saving and exact multi-element analysis, without the need for a work intensive sample preparation or time consuming system optimization, is therefore very important.

The multi EA® 5000 analysis system described in the following is well suited for the determination of the elements sulphur, nitrogen, carbon and chlorine in only one analysis cycle and is fully capable of meeting the continually increasing quality demands of the industry.

Figure 1. Multi-element analyser multi EA® 5000 with multi-matrix autosampler

Instrumentation

Analysis system

All measurements are performed with a multi-element analyser of the type multi EA® 5000 from Analytik Jena AG (see *Figure 1*) in the following configuration:

- multi EA® 5000 – basic device with double furnace
- Automatic Boat Drive – sample feed with flame sensor technology
- UV fluorescence detector - for the determination of sulfur contents
- Chemoluminescence detector - for the determination of nitrogen contents
- Micro coulometric chlorine module – for the determination of chlorine contents, as well as performing AOX, TOX, EOX analyses
- NDIR detector - for the determination of carbon content, as well as performing TOC analyses
- MMS 5000 – Multi-matrix sampler for the automatic introduction of solids and liquids, TOC, AOX, TOX and EOX samples
- GSS/LPG module for automatic introduction of gases, pressurized gases and liquefied gases

Sample Analysis

The determination of sulphur, nitrogen, carbon and chlorine content, as well as the determination of the environmentally relevant sum parameter EOX, is done in a two-phase process at 1050 °C, without the use of a catalyst. A multi-matrix sampler was used for automatic introduction of the liquid and solid sample matrices into the combustion furnace (see *Figure 1*).

In the first process phase, the evaporation of the sample substances in an inert gas atmosphere, and subsequent in an oxygen rich atmosphere the flame sensor controlled combustion of the gaseous components formed, took place.

In a second process phase, in a pure oxygen atmosphere, non-vaporizable sample components or cracking products of samples, which cannot be evaporated without sample decomposition, (e.g. crude oil, polymers, carbon, etc.) were quantitatively oxidized.

The gaseous reaction products, CO_2, NO_x, HCl and SO_2, formed during combustion are fed to the respective detection systems after the drying. The contents of sulfur, nitrogen and carbon are then determined simultaneously, therefore saving time. The determination of the chlorine content is performed afterwards, fully automatic in the same analysis sequence. Determination of the environmentally relevant parameters TOC and AOX is carried out in a fast, one-phase process at temperatures of 950 °C.

Element	Principle	Calibration substance	Detection limit
Sulphur	UVFD	Dibenzothiophene	10 µg/l
Nitrogen	CLD	Pyridine	30 µg/l
Carbon	NDIR	iso octane	100 µg/l
Chlorine	Coulometry	2,4,6-trichlorophenol	100 µg/l

Table 1: Detection limits of the detection systems used

No.	Sample	TC ± RSD	TS ± RSD	TN ± RSD	TSI ± RSD
1	Propylene	85.7 wt-% ± 0.1 %	520 µg/l ± 0.55 %	430 µg/l ± 5.15 %	130 µg/l ± 2.84 %
2	LPG	83.4 wt-% ± 0.1 %	5.6 mg/l ± 0.92 %	1.78 mg/l ± 2.27 %	180 µg/l ± 1.23 %
3	Benzene	92.2 wt-% ± 0.1 %	78 ppb ± 10.4 %	243 ppb ± 11.7 %	< 100 ppb
4	Iso octane	84.1 wt-% ± 0.2 %	< 10 ppb	46 ppb ± 26.8 %	< 100 ppb
5	Cumene	89.9 wt-% ± 0.1 %	56 ppb ± 7.1 %	89 ppb ± 0.6 %	333 ppb ± 8.6 %
6	Biodiesel	76.2 wt-% ± 0.3 %	960 ppb ± 0.63 %	1.95 ppm ± 2.54 %	< 100 ppb
7	Bioethanol	52.3 wt-% ± 0.1 %	700 ppb ± 1.4 %	68.9 ppb ± 12.4 %	< 100 ppb
8	Naphtha	74.8 wt-% ± 0.1 %	8.9 ppb ± 28.3 %	3.92 ppm ± 3.2 %	103 ppb ± 8.6 %
9	Gasoline	---*	5.2 ppm ± 2.9 %	1.36 ppm ± 2.1 %	254 ppb ± 2.5 %
10	Diesel	85.4 wt-% ± 0.2 %	2.8 ppm ± 2.5 %	850 ppb ± 4.03 %	120 ppb ± 1.1 %
11	Crude oil	95.2 wt-% ± 0.1 %	1.2 wt-% ± 1.3 %	0.13 wt-% ± 1.8 %	0.05 wt-% ± 1.2 %
12	Vacuum Residue	89.7 wt-% ± 0.4 %	8.7 g/kg ± 1.8 %	1.1 g/kg ± 2 %	15 ppm ± 1.8 %
13	Paraffin	84.3 wt-% ± 0.1 %	1.8 ppm ± 2.7 %	4.2 ppm ± 3.2 %	550 ppb ± 3 %
14	Coal	89.3 wt-% ± 1.4 %	183 ppm ± 2.3 %	0.39 wt-% ± 2.8 %	0.02 wt-% ± 1 %
15	Soot	100 wt-% ± 0.1 %	18 ppm ± 3.2 %	223 ppm ± 1.8 %	231 ppb ± 16 %
16	Polypropylene	---*	47.5 ppm ± 2.8 %	238 ppm ± 3.2 %	< 100 ppb

Table 2: Multi-element analysis of various petrochemical and chemical end products and raw materials.
** These parameters were not measured for the sample.*

Thanks to the excellent reproducibility of the method, a double determination is normally sufficient.

Calibration

Calibration of the analysis system is done with liquid standard kits. The solvent iso octane (see *Table 1*) is used as a matrix for the sulphur, nitrogen and chlorine standards or as standard substance for the carbon calibration.

For determination of the environmentally relevant parameter TOC, various concentrated aqueous solutions of potassium hydrogen phthalate were used.

The acting calibrations for the elements sulphur and nitrogen are shown in *Figure* 2.

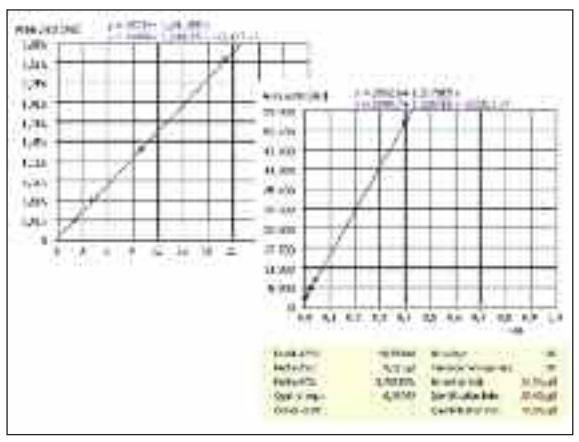

Figure 2. Calibration reports of various concentration ranges for the elements nitrogen and sulphur

The detection systems used show an outstanding linearity over a uniquely wide concentration range.

Based on the performed calibrations, the summarised detection limits for the tested elements are in *Table 1*. Calculation of these statistical characteristics was done by the multiWin® operating software from the calibration parameters, according to the requirements of DIN 32645.

Results and discussion

All analysed matrices are real samples coming from different industry branches. Samples 1 and 2 are gaseous, samples 3 to 13 are liquid, and samples 14 to 15 are solid matrices.

Results of the multi-element analysis of these samples are summarised in *Table* 2. *Table 3* contains the results of the determination of environmentally relevant sum parameters. Samples 17 to 20 are industrial wastewater and cooling water or disposal soil.

The carbon content of all examined samples is, determined by the organic origin of the analyzed matrix, between 52 and 100 %.

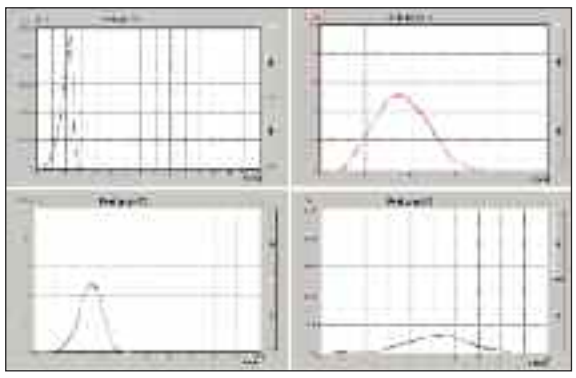

Figure 3. Measurement curves of the multi-element analysis from cumene

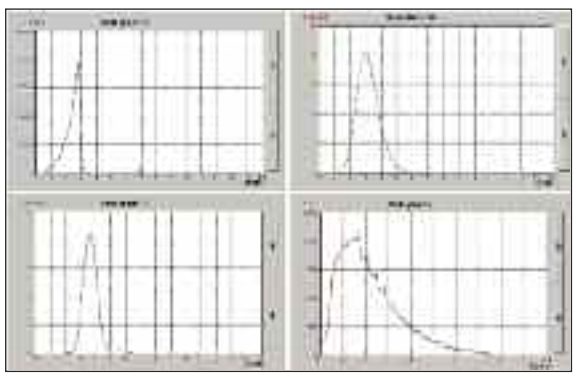

Figure 4. Measurement curves of the multi-element analysis of a crude oil

The N/S/Cl content of the tested petrochemical raw materials or waste products (crude oil, vacuum residue) are high, as expected, and reach into the mass percent range. *Figure 4* shows representatively for the measurement curves of the analysis of a highly viscose crude oil sample.

N/S/Cl contents in the trace and ultratrace range were present in the highly pure petrochemical end products (e.g. fuels, naphtha) or raw materials of the further processing industry (e.g. cumene, propylene). *Figure 3* is representative for the measurement curves of the aromatic hydrocarbon cumene.

Samples 17 and 18 are control samples of industrial process water. The parameters TOC, AOX were determined for them. Sample 19 and 20 are solid materials, for which the EOX content was determined.

The TOC content of both water samples was determined directly (NPOC mode).

The column method was used for the sample preparation for AOX determination. For the EOX determination the solvent n hexane was used for extraction (see *Table 3, Figure 5*).

Figure. 5 EOX analysis of disposal soil

The final examination of the results shows that the multi-element analysis with the multi EA® 5000, can be performed fast, uncomplicated and with outstanding precision, even for the most varied concentration ranges, from ultratraces up to mass percent, thanks to its high degree of automation in combination with modern wide range detection system.

Summary

Reaching a maximum of efficiency with the lowest costs is a continual effort in quality assurance. Especially for elemental analysis, this means that in the shortest time different elements can be fully automatically and simultaneously determined with only one analysis system.

To satisfy the continually increasing demands in elemental analysis, not only reliable combustion systems that guarantee a safe and quantitative oxidation of a broad spectrum of sample matrices are required, but also highly sensitive and also long-term stable detection systems, which can cover almost the entire concentration range.

The multi EA® 5000 offers all of this. Thanks to simultaneous/ sequential multi-element analysis, it combines short measurement times and low maintenance requirements with simpliest operation. This guarantees a trouble-free use in shift operation, which is required in modern labs and research facilities. The possibility to use one and the same analysis system furthermore for selected applications from the field of environmental and water analysis, allows an additional increase of effectiveness.

No.	Sample	TOC content± RSD	AOX content	EOX content
17	Cooling water	1.8 mg/l ± 1.2 %	5.8 µg/l	---*
18	Waste water	158 mg/l ± 0.3 %	92 µg/l	---*
19	Disposal soil A	---*	---*	1.38 mg/kg
20	Disposal soil B	---*	---*	109.1 mg/kg

Table 3: Determination of environmentally relevant sum parameters (TOC, AOX, EOX) for water and disposal samples
** These parameters were not measured for the sample.*