Fast and Reliable Chlorine Determination by Self-Adopting Systems

Dr. Stefan Jezierski, application chemist, Dr. Angela Gröbel, Product Manager, Analytik Jena AG
Konrad-Zuse-Str. 1, 07745 Jena, Germany
Email info@analytik-jena.com • Web www.analytik-jena.com • Tel +49 (0) 36 41 / 77-70

During storage, transportation and further processing, chlorine containing compounds can form harmful substances (HCl, metal halides …), which consume costly parts of the facilities (e.g. tanks, pipelines, catalysts). To avoid this, and to ensure a constant high quality and yield of the final products, it is crucial to control the chlorine content of the feeds and different process streams permanently. Therefore reliable results must be available in next to no time. This task is a real challenge for common techniques, since they are either limited to special matrix types or narrow concentration ranges. That's why numerous diverse techniques must be applied to cover the full range. This occupies not only manpower but also valuable time. A new generation of intelligent self-adapting analysers can produce the relief, which is urgently needed.

Chlorine is Everywhere

Chlorine is present everywhere in the world, whether organic or inorganic bound. Especially in refineries and petrochemical industry such materials can cause serious problems in numerous processes. This is the reason for monitoring chlorine constantly in feed materials, intermediates, final products, and waste and by-products. If the specified maximum permissible values are exceeded, not only the efficiency of plant will decrease but also the maintenance effort and costs (e.g. catalyst poisoning) will rise and the entire facility may suffer from considerable damages by corrosion and wearing.

In order to prevent such effects, a precise and quick determination is important. Depending on the matrices which have to be determined resp. the expected concentration range, many different, more or less automatable techniques were applied. Besides whet chemical methods coupled with ISE, photometry etc., and XRF, mainly combustion techniques (e.g. bomb, Schöninger) are in use. Among all these techniques, the high temperature combustion coupled with micro coulometric titration has proved to be most suitable. It delivers not only fast analysis and high sensitivity, but also a maximum degree of automation.

Optimum Combustion is the Base

As much as the concentrations differ (ppb – wt-%), as much the combustion behaviour of the varied matrices differs. Their volatility, boiling intervals and pyrolysis tendency are variable in a wide range. When analysing just one matrix type, this might not be a big issue, but for analysis of varied matrices manifold problems do appear.

The biggest challenge for sure is to create optimum conditions for sample digestion, and thereby, complete conversion of all sample components. Only this way it is possible to generate trustable results. Even the smallest amount of soot or cracking products will affect final results considerably. To avoid this, either plenty of time and experienced operators to create suitable combustion methods for each sample matrix are necessary, or just one auto-adaptive combustion system, which can be operated by everyone. Such optimisation can be realised by the flame sensor technology. It automatically adapts the combustion process to the special needs of each sample component and matrix type. Thus anybody can realise a quantitative combustion without any effort, independently from used sample quantities.

Table 1. Effects of different digestion modes on recovery of 100 µl 500 µg/l Cl reference matrix

Parameter	Boat program		
	CR boat	*Flame sensor*	*Adopted boat*
Analysis time	7 min	10 min	19 min
Chlorine content	321 µg/l	496 µg/l	512 µg/l
RSD	38.6 %	4.52 %	4.78 %

The manual or automatic fast introduction at constant rate (CR boat) cause incomplete combustion, low recovery and thus bad repeatability of the results. On contrary, low RSD and better recovery can be achieved using an adopted boat program (including waiting points and different rates), however very long analysis times are crucial to realise this. The flame sensor technology optimises introduction time and helps to achieve satisfying recovery and RSD at once.

Experimental

The samples were analysed without pretreatment using the multi EA® 5000 Cl in horizontal mode. The liquid and solid samples were dosed by means of a multi matrix sampler. Afterwards the transfer into the furnace was carried out fully automatically by means of a flame sensor controlled automatic

boat drive. The combustion takes place in a biphasic process. During the first phase volatile components were evaporated in an inert gas atmosphere and purged into the combustion zone, to be oxidised completely at 1050°C. In the second step remaining heavier sample components and possibly formed pyrolysis products, were combusted in pure oxygen. Before they were guided to the coulometer cell, the reaction gases, including HCl, are cleaned and dried by the auto-protection system and sulfuric acid. Meanwhile a powerful heating avoids condensation, which would affect Cl recovery remarkably. When HCl has arrived, it is absorbed in the cell electrolyte and titrated subsequently. An integrated cell cooling, drift control and usage of lightproof material, ensure a stable performance. This enables precise analysis results even for the lowest trace contents.

Fig. 1: multi EA® 5000 – automatic chlorine analysis system in horizontal mode

Fast and Reliable Results

When comparing the different materials, it strikes that result precision remains unaffectedly good independent of concentration and matrix type.

Thanks to the used wide-range coulometer, error-prone dilution of the higher concentrated samples can simply be avoided by cell extension. This allows direct analysis of Cl contents up to 10 % with surprisingly short measurement times.

Table 2: Results for the Chlorine determination

Sample ID	Sampling Mode	Quantity	c_{Cl}	RSD
Naphtha	liquid	100 µl	0.18 ppm	18.5 %
Gasoline	liquid	100 µl	1.73 ppm	2.00 %
Hydraulic fluid	liquid	50 µl	2.42 ppm	2.80 %
HCR feed	solid	50 mg	3.02 ppm	2.50 %
Crude oil	liquid, diluted	100 µl	750 ppm	2.30 %
Used oil	Solid	20 mg	0.04 mass-%	4.33 %
Catalyst	solid	20 mg	1.45 mass-%	1.83 %

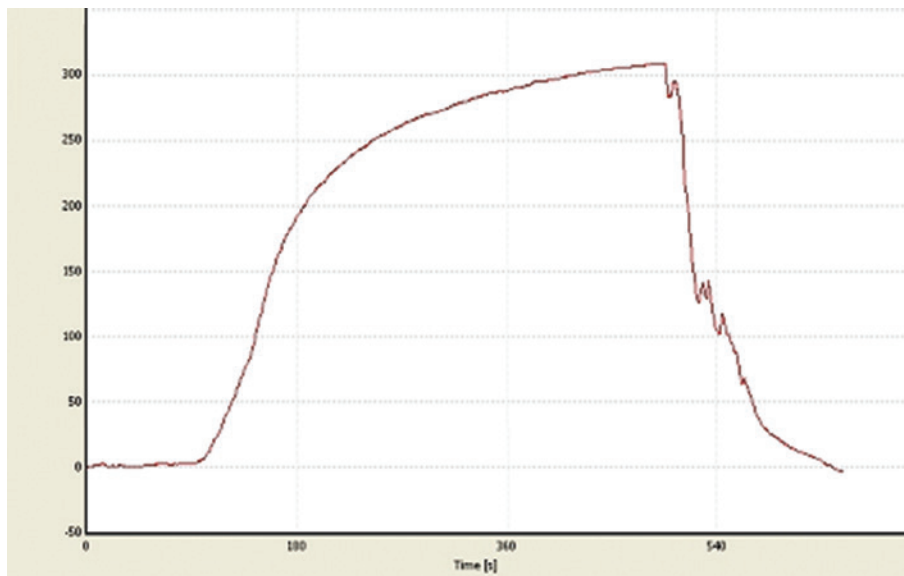Due to the matrix-optimised combustion, in most cases a triplicate analysis was sufficient.

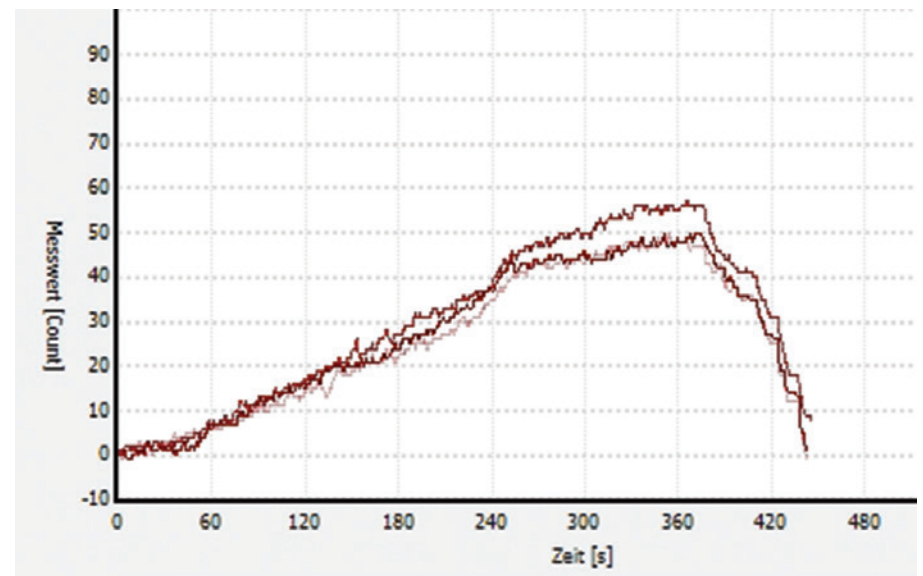*Fig. 2: Cl-determination of catalyst*

Fig. 3: Cl-determination of naphtha

Quick and Easy

As time and manpower in high throughput labs become more and more scarce, the need for quick and autonomous working analysis systems, requiring no permanent supervision, will increase constantly. Fully automatable, self-adapting analysers will satisfy this necessity. Multi EA® 5000 is such a system, combining fully time-optimised, matrix-independent quantitative combustion with a wide-range covering, highly sensitive coulometric titration.

Read, Print, Share or Comment on this Article at: Envirotech-Online.com/Articles