Determination of Total Chlorine in Derived or Secondary Fuels Using High-Temperature Combustion and Coulometric Titration

Introduction

Waste materials are becoming more and more important as valuable feed materials for energy production, as fuels and recycled feed materials for the chemical industry. To ensure a trouble-free processing and high quality of the final products, the exact elemental composition has to be determined. This is also crucial for avoiding the emission of undesired hazardous compounds.

In addition to heavy metals, carbon, hydrogen and sulfur, chlorine plays an important role. During processing, HCl can be formed and damage system components and contaminate costly catalysts. Under nonoptimal combustion conditions Cl compounds can influence the formation of extremely toxic dioxins. It's therefore important to know the exact Cl content of the matrix being used.

Due to the versatile properties of these matrices (inhomogeneous, vigorously reacting, nonvolatile, solid, highly viscose etc.), it is very difficult to ensure a quantitative determination of a representative sample aliquote. That's why classical methods, such as XRF, bomb method, etc., often fail or don't deliver satisfying results. An alternative for overcoming these problems is elemental analysis — using high-temperature combustion of the sample followed by coulometric titration of the formed HCl.

Challenge

Precise TCl determination for inhomogeneous, vigorously reacting organic matrices. Elimination of deflagration and soot formation despite high-temperature combustion of these matrices.

Solution

Controlled and quantitative combustion using flame sensor technology. Wide range coulometer technique with split mode for Cl determination from traces to wt%.

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Materials and Methods

Samples and Reagents

Six samples of different matrices were analyzed. Two, the oil sludge and the used grease, were paste like. The "ready to feed" sample was a solid brown powder. The refused derived fuels (RDF) and HWFS were fine-cut materials including fibers and plastic particles. The WWT, a paste-like material, contained larger particles.

Sample Preparation

The samples were analyzed directly, no sample preparation, such as homogenization, was required.

Calibration

The coulometric chlorine determination is an absolute method regarding Faradays Law. Therefore, the calibration of the analyzer is not necessary. The proper performance of the system (titration cell) was tested by means of an aqueous HCl solution with exactly known Cl content. For analysis in split mode, a split factor is required. This factor was also determined by means of the same HCl standard solution.

Instrumentation

The derived fuels have been analyzed with a multi EA® 4000 Cl elemental analyzer, equipped with wide range coulometer and split mode. The introduction of samples and the combustion control was realized with a FPG 48 solids autosampler and flame sensor technology.

The samples were weighted in quartz sample boats and then covered with a sufficient quantity of annealed ultra-pure quartz sand. These samples were transferred into the quartz combustion tube with the FPG 48, an intelligent combination of boat drive and solids autosampler. The transfer and combustion process was controlled by means of the flame sensor to avoid a too vigorous reaction and soot formation and thereby incorrect measurement results. In the first zone of the combustion tube, the samples are pyrolyzed in an inert argon atmosphere at up to 1050 degrees Celsius. In the second zone, the formed pyrolysis gases are oxidized in an oxygen-rich atmosphere at 1050 degrees Celsius. After a sufficient measurement gas cleaning from particles and the interfering combustion water, the yielded HCl gas was transferred either with or without split to the high concentration coulometer cell. Depending on the used mode and accessories, this Cl detector has an effective operation range from 0.3 µg to 10 mg chlorine. Here, the gases are absorbed completely in the cell electrolyte.

For the samples, amounts between 26 to 136 mg were used, depending on the expected Cl content.

Figure 1: multi EA® 4000 Cl with FPG 48

Method Parameters

Standard method settings from the method library were applied. The parameter settings for the combustion process and the sample transfer are summarized in table 1. The evaluation parameters for the detection of chlorine are given in table 2.

Table 1: Process parameters

Parameter	Specification
Temperature	1050 °C
Introduction Speed Program	organic
O_2 flow (combustion)	0.4 L/min
Ar flow (pyrolysis)	0.4 L/min

Table 2: Cl detection parameters

Parameter	Specification
Max. titration time	600 s
Titration delay	10
Cell temperature	20 °C

Results and Discussion

The results of the six derived fuel samples and one standard material summarized in table 3 show the averages of three replicate measurements. Due to the matrix-optimized combustion, in most cases a threefold determination is sufficient to achieve satisfying results even for such challenging inhomogeneous multi-component matrices. This remarkably affects the sample processing time and allows for a higher sample throughput. The overall performance of the analysis system was validated by analyzing a Cl material with known concentration (HCl standard solution).

Table 3 shows the results of the chlorine detection. Given are the weight of the samples, the result in mass% and the absolute deviation of the single measurements (SD). Each sample was measured at least three times.

Table 3: Results of the chlorine detection in derived fuels

Sample ID	TCl	SD	Sample mass
WWT	0.012 %	± 0.001 %	129–136 mg
Sludge Oil	0.504 %	± 0.035 %	17–21 mg
Ready to Feed	0.106 %	± 0.008 %	44–63 mg
RDF	0.334 %	± 0.041 %	26–34 mg
Used Grease	0.014 %	± 0.001 %	98–185 mg
HWFS	0.437 %	± 0.029 %	26–33 mg
Cl Standard 0.354 %	0.357 %	± 0.009 %	26–33 mg

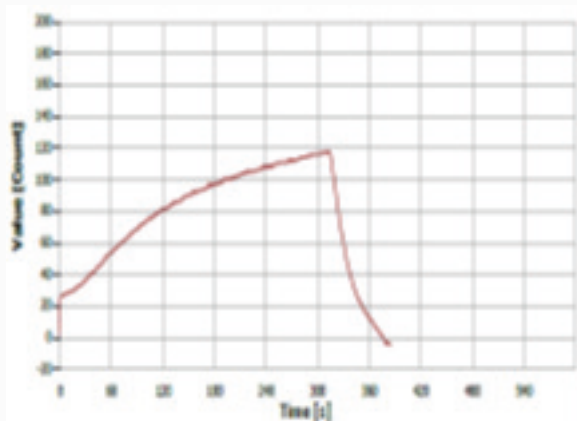Typical measuring curves for the six given samples are depicted in Figures 2–7.

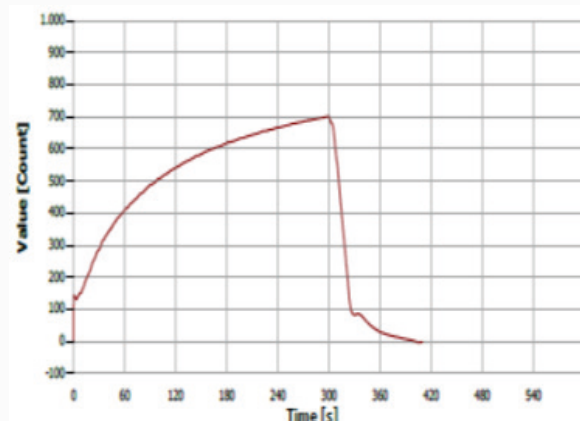Figure 2: TCl measuring curve for sample WWT

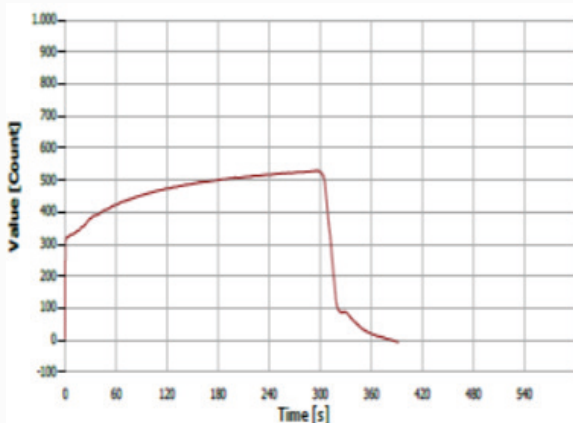Figure 3: TCl measuring curve for sample sludge oil

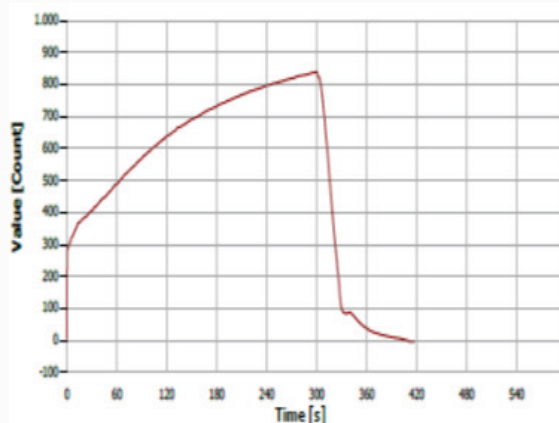Figure 4: TCl measuring curve for sample ready to feed

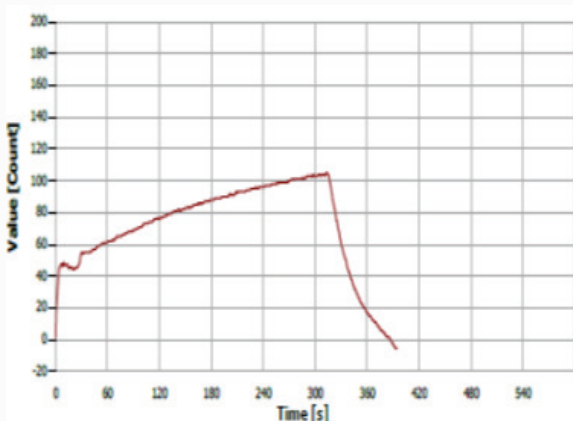Figure 5: TCl measuring curve for sample RDF
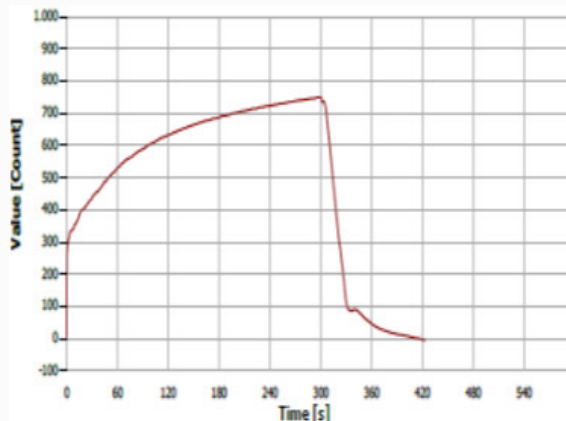
Figure 6: TCl measuring curve for sample used grease

Figure 7: TCl measuring curve for sample HWFS

The entire analysis process is divided in two major parts. The safe, flame sensor controlled, and thereby soot-free, digestion of the different sample matrices (pyrolysis, oxidation, absorption of HCl in titration cell) consumes the biggest part. It's not possible to speed up the transfer and still ensure a safe and quantitative sample combustion. Titration makes up the second part of the process. With its < 2 min duration, it's extremely fast, thanks to fully automatic dynamic adaptation of the titration current to the present Cl content.

Conclusion

The multi EA® 4000 facilitates safe and matrix-optimized determination of chlorine contents in inhomogeneous, vigorously reacting and difficult-to-digest organic sample matrices, such as derived fuels, used oils, polymer waste, lumber, etc. The used high concentration cell that is emplyed enables an extremely wide operation up to 10 % Cl (split operation). For challenging trace applications, the sensitive cell can alternatively be used.

Compared to the pre-programmed parameter mode, the classical principle of introduction, flame sensor technology is the better choice. Since position, speed, and waiting times are empirically defined by a skilled operator, the classical method is rather difficult to operate for such versatile and reactive organic matrices. By contrast, flame sensor technology enables a safe and optimum combustion independent of operator skills and matrix composition.

The titration cell and its patented three-in-one ceramic electrode are robust, low-maintenance components. This allows for easy operation with minimum downtime for maintenance, even by non-experts.