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

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

Determination of Total Chlorine in Solid Recovered Fuels Using High-Temperature Combustion and Coulometric Titration

Introduction

Waste materials with a high proportion of organic constituents, such as plastics, sewage sludge or oil sludge and used wood are becoming more and more important as valuable substitute fuels for energy production and recycled feed materials for the chemical industry. During combustion of such materials especially chlorine compounds have a negative impact. The formed HCl gas and resulting inorganic chlorides contribute in corrosion, clogging, and fouling processes in the combustion system.

In addition, dioxins, which can also be formed during the combustion of organic materials in the presence of chlorine, are a danger to humans and the environment.

These so-called solid recovered fuels (SRF), also adressed as refuse derived fuels (RDF), are frequently used in the cement industry or in power plants for the generation of electricity and district heating. It's therefore important to know the exact Cl content of the derived fuels being used.

The analysis of the halogen and sulfur content in solid recovered fuels is described in DIN EN 15408[1] and the characterization of waste in DIN EN 14582[2]. In each case, combustion in an oxygen atmosphere in a closed system is described, followed by various detection methods. In addition, alternative, direct automated techniques are also permitted. Due to the versatile properties of SRF (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 digestion 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 coupled with direct automatic coulometric chlorine determination. The total chlorine content is quantified directly from the original sample without additional sample treatment steps.

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The multi EA 4000 combustion elemental analyzer offers a wide operation range starting from limit of detection of 0.3 ppm up to 10% chlorine in split operation. Typical measurement times per sample are between 3 and 10 minutes. The durable instrument design makes it the perfect match for industrial QC labs (at-line) and classical contract labs (offline).

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 refuse derived fuels (RDF) and HWFS were fine-cut materials including fibers and plastic particles. The WWT, a paste-like material, contained larger particles. For the samples, amounts between 26 to 136 mg were used, depending on the expected Cl content.

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 the multi EA 4000 Cl combustion elemental analyzer, equipped with wide range coulometer and split. The introduction of samples and the combustion control was realized with a programmable FPG 48 solids autosampler. Alternatively also the flame sensor technology can be applied.

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 can be controlled by means of pre-programmed parameter sets of the method library or automatically, by the optional flame sensor. Therefore too vigorous reaction and soot formation and thereby incorrect measurement results can be avoided. In the first zone of the combustion tube, the samples are pyrolyzed in an inert argon atmosphere at up to 1,050 °C. In the second zone, the formed pyrolysis gases are oxidized in an oxygen-rich atmosphere at 1,050 °C. Afterwards the measurement gas is dried and possibly formed particles are removed sufficiently to prevent interferences and analyte loss. The yielded HCl gas was transferred either with or without split to the high concentration cell, where it is absorbed completely in the cell electrolyte. Depending on the used mode and accessories, an effective operation range from 0.3 µg to 10 mg chlorine can be covered.

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 and 3. The evaluation parameters for the detection of chlorine are given in Table 2.

Table 1: Process parameters

Parameter	Specification
Temperature	1,050 °C
Introduction speed program	Organic / flame sensor
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 4 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 4 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. Typical measuring curves for the given samples are depicted in Figures 1–6 on the following page.

Table 4: Results of the chlorine determination in derived fuels

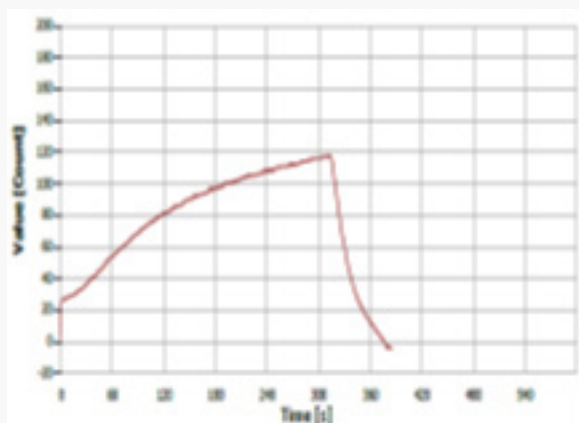| Sample ID	TCl	SD	Sample mass
WWT	0.012%	± 0.001%	129–136 mg
Sludge Oil	0.504%	± 0.035%	17–21 mg
"Ready to Feed"	0.106%	± 0.008%	44–63 mg
RDF	0.334%	± 0.041%	26–34 mg
Used Grease	0.014%	± 0.001%	98–185 mg
HWFS	0.437%	± 0.029%	26–33 mg
Cl Standard 0.354%	0.357%	± 0.009%	26–33 mg

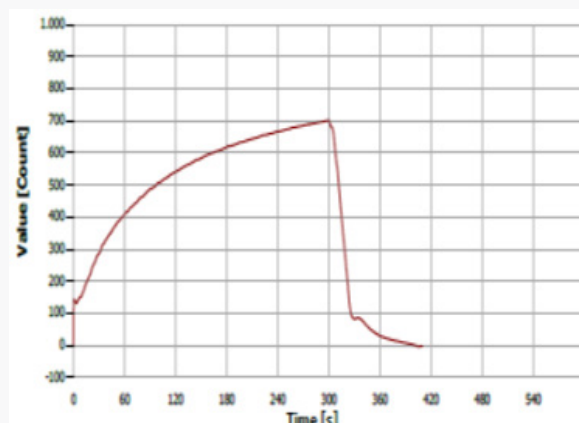Figure 1: TCl measuring curve for sample WWT

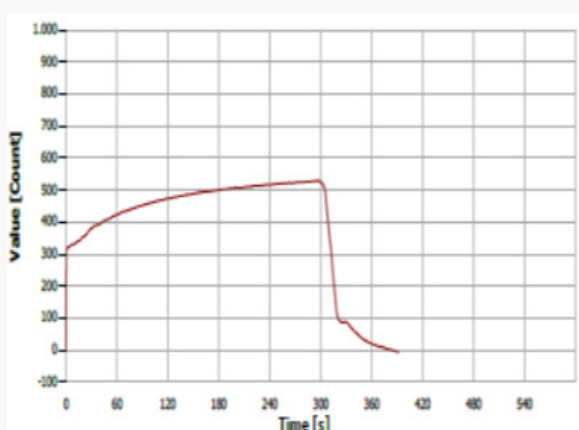Figure 2: TCl measuring curve for sample sludge oil

Figure 3: TCl measuring curve for sample "Ready to Feed"
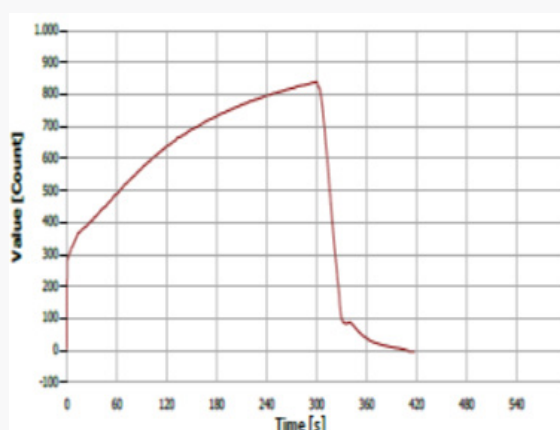

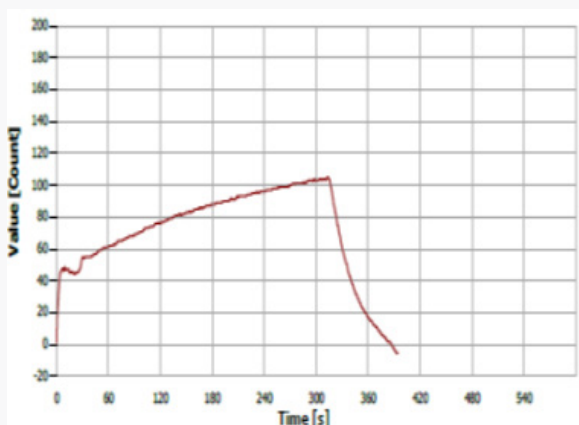Figure 4: TCl measuring curve for sample RDF
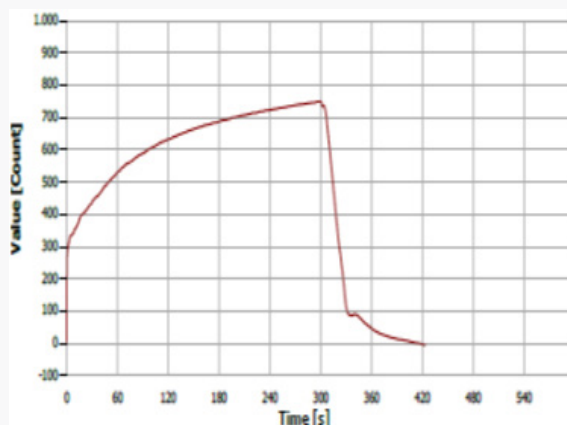

Figure 5: TCl measuring curve for sample used grease

Figure 6: TCl measuring curve for sample HWFS

The major part of the analysis time is occupied by the safe an controlled sample supply and combustion, the gas purification and adsorption of the formed HCl gas in the cell electrolyte. Compared to this the actual detection of the chlorine by coulometric titration, with its less than 2 minutes duration, is extremely fast. This is ensured by fully automatic, dynamic adaptation of the titration current to the present Cl content.

As combustion and sample transfer is optimized to the specific matrix needs, it's not possible to speed up the process and still ensure a safe and quantitative sample combustion.

Conclusion

The multi EA 4000 facilitates safe and matrix-optimized determination of chlorine contents in inhomogeneous, vigorously reacting and difficult-to-digest organic matrices, such as derived fuels, used oils, polymer waste, lumber, and many more. The used high concentration cell that is employed enables an extremely wide operation range up to 10% Cl (split mode). For challenging trace applications, a special „sensitive" cell can be used alternatively.
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. Compared to other applicabale detection principles like IC or ISE this is a clear advantage. The pre-programmed parameter mode (method library), optimized to the needs of organic matrices by our experts, is the classical principle of introduction.
Since position, speed, and waiting times are pre-defined, no empiric method development by the operator is required.
For suited sample matrices alternatively flame sensor technology can be applied.

Figure 7: multi EA 4000 Cl with FPG 48

References

[1] EN 15408:2011-05 Solid recovered fuels - Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content

[2] EN 14582:2016-12 Characterization of waste - Halogen and sulfur content - Oxygen combustion in closed systems and determination methods