Challenge

Precise TCl determination in plastic materials.

Solution

Direct analysis via quantitative combustion using an automated Cl analyzer with intelligent sample supply technology and coulometric detection.

Direct Total Chlorine Determination in Plastic Materials

Introduction

Mixed plastic waste has become an important refuse derived fuel for energy production. Further, it is considered a valuable raw material to the recycling industry helping to reduce the amount of virgin plastic materials produced.
Understanding the proportion of PVC (polyvinyl chloride) in mixed plastic wastes is essential analytical task, as the chlorine contained in PVC is an undesirable constituent. 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.

In order to prevent this, it is crucial to determine the chlorine content precisely and quickly. For this purpose a multitude of methods are available which require high effort, reflected by processing times and missing ease of use. Often a full automation of analysis process, from sample supply over digestion till the detection, is barely realizable.
Combustion elemental analysis is offering direct automatic chlorine determination, as mentioned in EN 15408, as a superior alternative to these methods.

The multi EA 4000 Cl enables direct analysis of total chlorine content in polymeric and other challenging organic materials, providing a novel, simple and cost-effective analytical approach (proof-of-principle). A high-temperature combustion step of plastics in oxygen is followed by automatic micro-coulometric titration of formed HCl. The total chlorine content is quantified directly from the original sample without additional sample treatment steps.

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 lay between 3 – 10 min. The robust instrument design makes it the perfect match for industrial QC labs (at-line) and classical contract labs (offline).

Materials and Methods

Samples and Reagents

Two shredded plastics samples that were already ground and sieved (particle size ≤ 1 mm) to form homogeneous grey and fluffy solid samples, were submitted to analysis. Sample aliquots between 45 to 56 mg were used for analyses.

Sample Preparation

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

Calibration

The coulometric chlorine determination is an absolute method regarding Faraday`s 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 shredded plastics were analyzed with a multi EA 4000 Cl combustion elemental analyzer, equipped with wide-range coulometer and split.

Initially, the shredded plastics samples were weighed in quartz sample boats and then covered with annealed ultra-pure quartz sand. The so-prepared samples were transferred automatically into the quartz combustion tube of the multi EA 4000 Cl by the FPG 48 solids autosampler, and combusted in a controlled manner, following a pre-programmed parameter set of the instrument´s method library. Hence, slow and complete reaction is ensured, that allows soot-free operation and accurate results.

In the first zone of the combustion tube, the samples are pyrolyzed in an inert argon atmosphere at up to 1050 °C. In the second zone, the formed pyrolysis gases are oxidized in an oxygen-rich atmosphere at 1050 °C. Afterwards the measurement gas is dried and possibly formed particles like ash are removed sufficiently to prevent interferences and analyte loss. The yielded HCl gas was transferred, either with or without applying the 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.

Figure 1: Recommended system configuration: 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 and 3. The evaluation parameters for the detection of chlorine are given in Table 2.

Table 1: Process parameters

Parameter	Specification
Temperature	1050 °C
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

Table 3: FPG 48 parameter set

Speed [mm/min]	Position [mm]	Specification
500	75	0
100	180	180
100	325	0

Results and Discussion

The results for the shredded plastic samples and one standard material with known chlorine content are summarized in Table 4 and reflect an average of three replicate measurements per sample. A threefold determination per sample is recommended for such kind of inhomogeneous multi-component matrices to achieve best analytical results. The good match of the measured chlorine content and nominal value of the standard material proves the excellent overall performance of the analysis system.

Table 4: Results of the chlorine determination in plastic materials

Sample ID	TCl [g/kg]	SD [g/kg]	Sample mass
Shredded plastics 1	7.79	± 0.20	45 – 56 mg
Shredded plastics 2	10.94	± 0.76	45 – 56 mg
Cl Standard (35.45 g/kg)	35.31	± 1.17	50 mg

The combustion behavior of both shredded plastic samples was very good. The chosen sample amount combusted smoothly and without soot formation. This is reflected by relatively small deviation of results for replicate runs.

Typical measuring curves for a shredded plastics sample and the standard material are depicted in Figure 2 and Figure 3, respectively.

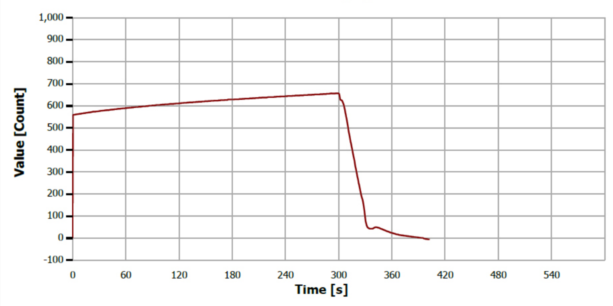

Figure 2: TCl measuring curve for sample “shredded plastics 2”

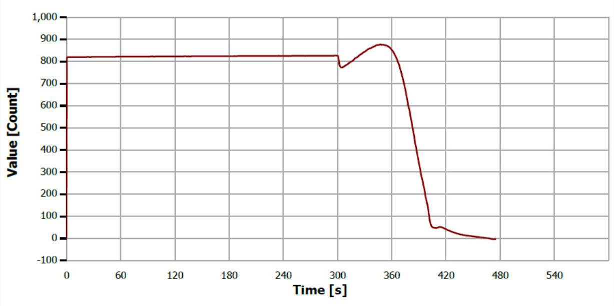

Figure 3: TCl measuring curve for standard 35.45 g/kg

The rate-determined step for the analysis of shredded plastic materials is the controlled sample supply and steady combustion, the gas purification, and subsequent adsorption of the formed HCl gas in the cell electrolyte. The chlorine detection by coulometric titration in turn takes less than 2 min due to a fully automatic and dynamic adaptation of the titration current to the present Cl content. The resulting total time per sample replicate is about 10 minutes.
As combustion and sample transfer is optimized to the specific matrix needs, it is not possible to speed up the process without compromising safety and quantitative sample combustion.

Conclusion

The multi EA 4000 combustion elemental analyzer facilitates the safe and accurate determination of chlorine contents in shredded plastic materials. Grinded and sieved sample amounts about 50 mg can be submitted to chlorine analysis directly thanks to the FPG 48 solid sampler. The sampler transports the samples into the combustion tube using a predefined parameter set of the analyzer`s method library, applicable for reactive organic matrices such as plastic samples. Since position, speed, and waiting times are predefined, operators are not required to conduct further method development.

The multi EA 4000 analyzer is equipped with titration cell and robust three-in-one ceramic electrode patented to Analytik Jena. It is optimized for robustness, low maintenance and high ease of use for any operator´s skills level and lab environments. Besides, the high concentration cell enables an extremely wide operation range up to 10% Cl (in split mode).

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