Chlorine Determination in Fatty Acids, Paraffins and Polymers with the aid of High Temperature Combustion Analysis

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Introduction

The analysis of organic solids, such as paraffins, fatty acids and polymers, represents a special challenge for modern analytical systems. Whereas liquids can be injected directly into the system using a syringe, solids generally have to be inserted on a tray. As many organic solids are mixtures of substances with different melting and boiling ranges, controlled sample insertion, combined with intelligent, flame sensor controlled oxidation, is required.

Fatty acids, paraffins and polymers

At room temperature, fatty acids exist in liquid, paste or solid form. The different degrees of hydration determine the melting and boiling points. Typical melting point ranges lie between 10 °C and 80 °C, the boiling point range generally above 100 °C. Fatty acids are catalytically hydrated to alcohols on an industrial scale. Too high chlorine concentrations cause catalyst poisoning.

The aggregate state of paraffins is essentially determined by their composition (chain length). They are classified according to their melting range and viscosity (paraffin oil, white oil) soft paraffin, petrolatum (Vaseline) and hard paraffin. Paraffins are mainly used in the production of cosmetics (e.g. cremes) and waxes (e.g. candles). Exacting demands are therefore placed on their purity and composition, which are satisfied with continuous product monitoring.

Polymers (PP, PE, PS, etc.) are characterized by their different molecular chain lengths and branching. Their properties are essentially influenced by the purity of the monomer source materials and the additives (flame protection, propellant, IR absorber, adhesion promoters, etc.) and dyes. Contamination and additives can also contain chlorine. To ensure that the end product also satisfies the quality requirements, the chlorine content is monitored during the production process.

Analysis system

All measurements were carried out with an element analyzer of the type multi EA 3100® (Fig. 1) in the following configuration (Fig. 2):

- multi EA 3100® basic instrument in horizontal operating mode
- “High sensitive” and “sensitive” chlorine modules for the microcoulometric determination of chlorine content in the trace range
- Automatic tray insertion system with flame sensor technology

Fig. 1 multi EA® 3100 elemental analyzer

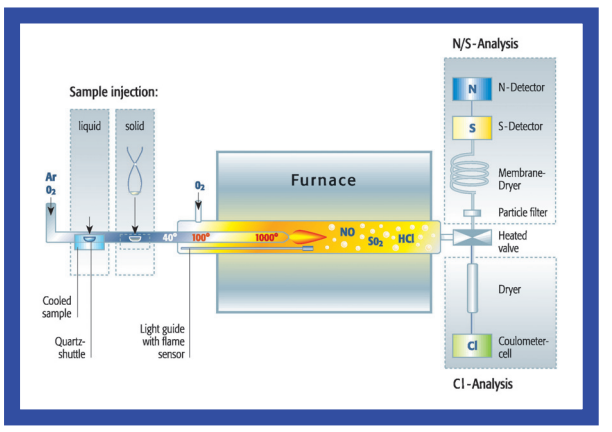

Fig. 2 The principle of high combustion analysis with multi EA® 3100

Coulometric detectors for chlorine determination

Various chlorine modules are available for the system, which can be deployed according to the measuring range of interest. The “Cl – high sensitive” module, which is specially designed for trace analytics, is particularly well suited for the analysis of fatty acids. The “Cl – sensitive” module, equipped with a zero-maintenance combination electrode, is especially well suited for paraffin and polymer analytics. This module is mainly used in the ppm range. A combination module can be used for all possible matrices. Polymer compounds with a high chlorine content may be conveniently detected with the “Cl – high concentration” option without having to frequently change the electrolyte.

Chlorine module	Application in solid analytics
C l - high sensitive	fatty acids paraffins
Cl sensitive	paraffins polymers
C l - high sensitive/sensitive	all matrices inve
Cl – high concentration	polymers and other substances with a high chlorine content

Intelligent combustion of fatty acids, paraffins and polymers

Owing to the special difficulties with the melting and boiling point range, two-phase sample insertion is recommended: In the first phase the sample is transferred to the melting zone and remains in this zone (waiting position) until the sample has been converted to the liquid phase. In the second phase the now liquid sample is checked, vaporized and finally oxidized with the aid of a flame sensor. This form of intelligent sample insertion has proven itself both in fatty acid analytics, as well as in paraffin and polymer analytics, and is effective in preventing the otherwise common complication of system sooting. It also turns out to be the only practicable soot-free method for many samples and sample mixtures.

The otherwise common continuous sample insertion method often unavoidably leads to spraying of the sample for this matrix and to sooting of the system.

Method parameters

Parameter	Setting
Oxygen	200 ml/min
Argon	200 ml/min
$T_{furnace}$	1,050 °C
Combustion regime	flame sensor controlled combustion with waiting position
$t_{combustion}$	120 - 300 s
Detection Cl	coulometric titration

Results

The samples were separately weighed out, measured and the standard deviation determined. The “high sensitive“ chlorine cell is suitable for chlorine determination of paraffin and fatty acids and can also be used below 1 ppm chlorine. The “sensitive” cell was used for polymer analytics.

Sample	Cll [mg/kg]	RSD [%]	Chlorine module
Paraffin sample 1	0.33	11.42	“high sensitive“
Paraffin sample 2	0.52	8.01	“high sensitive“
Paraffin sample 3	0.72	7.02	“high sensitive“
Fatty acid sample 1	0.16	16.78	“high sensitive“
Fatty acid sample 2	0.40	6.41	“high sensitive“
Fatty acid sample 3	5.40	3.41	“high sensitive“
Polymer sample 1	471.0	4.7	“sensitive“
Polymer sample 2	461.1	5.2	“sensitive“
Polymer sample 3	416.7	4.9	“sensitive“

Conclusion

All samples investigated melted completely in the waiting position, before the flame sensor program performed the controlled vaporization and combustion. The samples could therefore be analyzed without special adaptation of the method. Sample carry-over was largely avoided by automatically baking out the tray in a stream of oxygen.