Challenge

Analysis of TN in difficult to digest, highly viscous sample matrices

Solution

High temperature combustion within O_2^+ parameter mode for optimal digestion of the sample followed by chemoluminescence detection (CLD)

Heavy Fuel Oil, Feed Materials and Residues – Trustable Determination of High Nitrogen Contents in Viscous, Complex Matrices

Introduction

The worldwide growing demand for energy and the fact that the easy-to-find and cheap crude oil reserves are basically gone, force oil companies to process heavy crude oil and heavy fractions of the refining process (e.g. distillation residues, heavy fuel oil etc.) in an increasing extent.

Heavy fractions, as thick as molasses, are not only difficult to transport and handle, but also require advanced strategies for the compulsory quality control. For such matrices especially the nitrogen content is of interest due to its negative effects on the refining process (e.g. by poisoning of catalysts, unwanted side-products etc.).

The TN determination by means of high temperature combustion followed by chemoluminescence detection (CLD) is approved for analysis of light fractions like naphtha, gasoline, heating oil. The nitrogen compounds present are easy-digestable pyridine and quinoline derivatives. The heavier the fraction, the higher is the content of more complex, poly-condensed nitrogen compounds (e.g. porphyrin). When being analyzed with the same method, these matrices deliver up to 25 % too low results for TN.

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The typical boiling points of above 400 °C and relatively high nitrogen content exceeding 0.5 wt% make the investigation of these materials non-trivial. A dilution step before analysis to decrease the extremely high nitrogen content is often applied for small improvement, but it cannot eliminate this effect. An additional optimization of the digestion process is required to maximize the recovery up to ratios between 95–100 %. For this purpose we have developed the O_2^+ parameter mode.

Instrumentation

The multi EA 5100 equipped with chemoluminescence detector covers a unique wide measurement range from ultra-trace contents (10 ppb) up to the weight percent range (1 wt%). The flexible adaptation of the sample volume (1–100 µL), based on the expected nitrogen content, allows the operator to benefit from high precision combined with short analysis times.

The analyses have been run with the multi EA 5100 with automatic boat drive ABD in the horizontal operation mode. The multi matrix sampler MMS equipped with liquids kit was used for the fully automatic injection of 10 µL of the dilutions. The samples were decomposed at 1050 °C catalyst-free in a two-phase combustion process. To ensure an optimal digestion even of complex compounds such as porphyrin, the O_2^+ parameter mode was applied (see Table 1). In this mode, additional oxygen is already present during the evaporation of the sample matrix at lower temperatures. The ABD parameter program used, consists of three waiting positions and is presented below in Table 1. Due to the waiting and the slow rate of sample boat introduction into the combustion tube, the evaporation is slowed down remarkably. This ensures optimal conditions for the conversion of even challenging nitrogen compounds, thus improves the yield of the NOx compared to unwanted side products such as N_2O and N_2, which cannot be detected by the chemoluminescence.

The generated reaction gas was dried and purified, before the included NOx was quantified by means of a chemoluminescence detector (CLD).
Thanks to the excellent reproducibility, a triplicate analysis was sufficient to achieve reliable results.

Table 1: O_2^+ parameter mode – ABD parameter set

Waiting Positions	Speed	Stop Position	Waiting Period
1	600 mm/min	100 mm	0 s
2	60 mm/min	180 mm	0 s
3	30 mm/min	307 mm	0 s

Samples and Reagents

Sample Preparation

The provided samples were dark-colored and high-viscous oil samples (VGO, HCR feed etc.). All were diluted to enable a comforTable sample introduction by means of the autosampler as well as to allow optimal conversion of the included complex nitrogen compounds. To get homogeneous aliquots, the samples were heated up in a water bath (80 °C, 10–15 min) and afterwards they were shaken thoroughly. Then dilution of the samples was done to the level of 50 mg/kg by using o-xylene as solvent.

Calibration

The calibration of the multi EA 5100 was carried out by different concentrated liquid standards (0–75 ppm N), based on acridine in o-xylene.

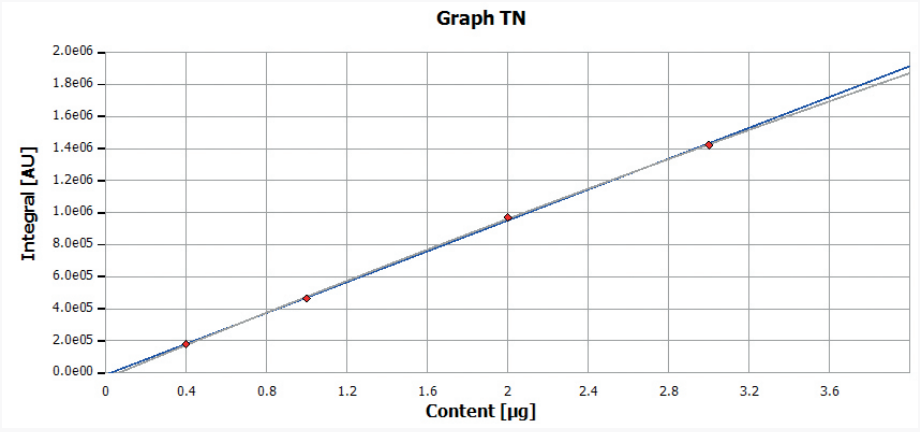

Figure 1: Calibration curve of acridine in o-xylene, calibration range 10 – 75 ppm N

Results and Discussion

In Table 2 the results gained by using a common procedure resp. the O_2^+ parameter mode are compared. The corresponding TN analysis curves are shown in Fig. 2 – 4.

Table 2: Results of TN determination by means of different strategies

Sample	TN nominal	Recovery	
		Common procedure	O_2^+ parameter mode
Residual fuel 1	0.64 wt-%	73 %	95 %
Residual fuel 2	0.70 wt-%	71 %	97 %
Heavy fuel oil	0.50 wt-%	75 %	100 %

When using the O_2^+ parameter mode acceptable high recovery rates can be gained with a good reproducibility, even for difficult to digest matrices.

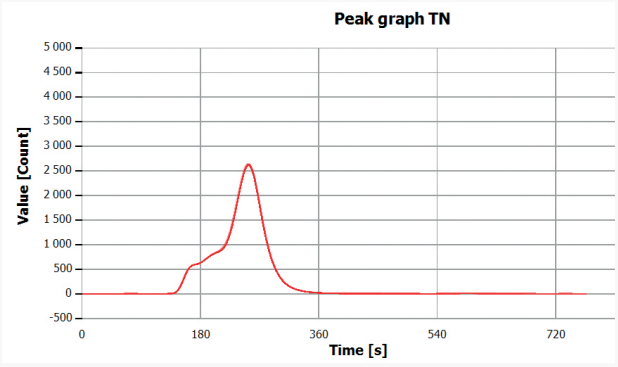

Figure 2: TN determination "residual fuel 1"

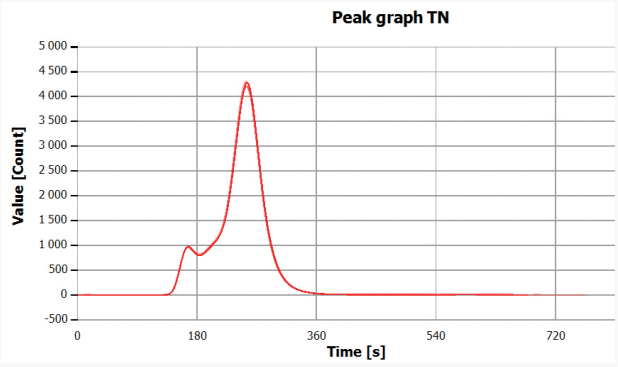

Figure 3: TN determination "residual fuel 2"

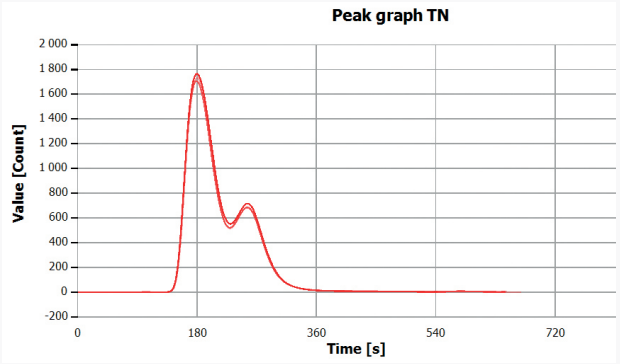

Figure 4: TN determination "heavy fuel oil"

Conclusion

The multi EA 5100 in combination with the O_2^+ parameter mode guarantees best results for the TN measurement of difficult to digest, highly viscous sample matrices such as VGO, heavy fuel oil, residues etc..
The multi EA 5100 can be upgraded with suitable accessory modules for automatic determination of Sulfur (TS), Chlorine (TX) and Carbon (TC) in solid, liquid, gaseous and LPG sample matrices.

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