# Nitrogen Determination in the Times of Scarcity of Natural Resources

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**Crude oil is a fossil fuel that was naturally formed during millions of years in the interior of the earth and has been known and used by mankind since ancient times. Crude oil has become of great importance since the invention of the internal combustion engine and the rapid industrial development by the late 19th century. Start of commercial drilling and production of petroleum in the mid-1850s, led to their widespread adoption in a variety of applications**

Crude oil is a mixture of hydrocarbons of various molecular weights and variable amounts of sulphur, nitrogen, and oxygen compounds. It is normally not used directly as fuel or as raw material for the production of chemicals. Several steps of refining, including distillation, cracking, treating and reforming, are required first to separate the crude oil into simpler fractions that can be further used as fuels, lubricants, or as intermediate feedstock to the petrochemical industries. [1]

Furthermore, the presence of different types of impurities makes the direct consumption of crude oil inappropriate. Such components like water, acid, sulphur- and nitrogen-containing molecules, heavy metals etc. can lead to rapid corrosion of extraction, transportation and storage equipment.

Organic nitrogen compounds occur in crude oils either in a simple heterocyclic form as in pyridine (C5H5N) and pyrrole (C4H5N), or in a complex structure as in porphyrin. These compounds are rather stable due to their aromatic nature. Nitrogen compounds contribute serious problems both for producers and consumers, in particular the poisoning of catalyst during the refining processes, and the degradation observed in fuels during storage and handling, as well as NOx emissions from fuel combustion. Organic nitrogen compounds strongly adsorb on catalyst active sites and inhibit the removal of both nitrogen- and other heteroatom-containing compounds during hydrotreatment. Basic nitrogen compounds (pyridinic forms), even at levels of a few tens of ppm, are believed to severely inhibit hydrodesulphurization. [2]

Thus, the information about the composition of crude oil, intermediate and final products along the refinery process is essential for establishing a processing strategy.

A common technique for determination of nitrogen content is chemiluminescence detection (CLD). During the high temperature combustion of a nitrogen-containing sample in oxygen atmosphere, the total nitrogen in the measuring gas is present as NOx (NO and $NO_2$):

$$R\text{-}N + O_2 \rightarrow NOx\ (NO, NO_2\ldots) + CO_2 + H_2O \qquad (1)$$

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad (2)$$

$$NO_2^* \rightarrow NO_2 + h\nu \qquad (3)$$

To have $NO_2$ content usable for the detection, the measuring gas is led through a converter which reduces $NO_2$ to NO. Next the NO oxides are exposed to $O_3$ which is generated from the fed $O_2$, within the device itself. During this reaction, $NO_2^*$ in excited state is generated temporarily (2), which emits electromagnetic radiation in the range of visible light when passing into its original state (3). The emitted light quantity is proportional to the $NO_2^*$ concentration and, thus, the detected light is a measure for the concentration. Only NO is involved in the reaction which makes the method very selective and free of influences of other components in the measuring gas.

### Experimental

Measurements of total nitrogen content were performed using an elemental analyzer multi EA® 5000 (Fig. 1). Two steps of combustion at 1050°C, first in argon (pyrolysis step) and then in oxygen (oxidation step) atmosphere, is used for digestion of samples. Depending on the matrix, sample introduction is implemented using a boat inlet in horizontal mode, or direct injection in vertical furnace configuration. In case of high viscous, intensive colored samples with high content of nitrogen, such as heavy petroleum fractions and residues, horizontal mode with the Flame Sensor Technology is an optimal solution. This technique ensures an optimized and complete combustion process due to controlled introduction of samples into the furnace, soot formation is thus prevented.

Calibration of the system is commonly made using liquid calibration standards based on pyridine dissolved in iso-octane or acridine in o-xylene in the range of interest.

For introduction of liquid and solid samples, as well as for performing a calibration, the automatic multi matrix sampler MMS 5000 was used. It ensures high precision of dosing and facilitates automation in routine analysis. The sampler can be used for the vertical and the horizontal furnace mode. After the combustion process and steps of purification and drying the analyte gas is directed towards the CLD module for detection.

Comfort and safety of the system's performance is ensured via a number of integrated sensors which are permanently monitoring all important parameters of the system such as gas flows, tightness, internal pressure, temperature and so on.


*Fig. 1: multi EA® 5000*

### Investigation of complex matrices

The composition and quality of oil found in different regions of the world can vary significantly. The lighter grades of crude oil produce the best yields of fuel products. However, the world's major oil companies all suffer from the fact, that the world's cheap, easy-to-find crude oil reserves are basically gone. [3] Oil refineries increasingly have to process heavy oil and bitumen, and use more complex and expensive methods to produce the products required. [1]

Because of the increased thermal stability of nitrogen compounds they are concentrated in such heavier petroleum fractions and residues. The typical boiling points of >400°C and relatively high nitrogen content exceeding 0.5 wt.% make the investigation of these materials non-trivial. Preliminary dilution with an appropriate solvent is often inevitable. Furthermore, a modified combustion process was shown to contribute to the better digestion of such "difficult" matrices. Mentioned above two steps combustion process used in multi EA® 5000 includes in this case so called additional oxygen flow that is mixed together with argon applied for the first, pyrolysis step of combustion. The relationship in the mixture of Ar and $O_2$ was set to 3:1. Since the dilution of the samples with o-xylene was found to deliver best analysis results, the calibration of the system was done using standards on the basis of this solvent.

Several high viscous and intensive colored solid-like residual fuel samples were investigated using multi EA® 5000. In the table below a comparison of results got using a common procedure (e.g. without additional oxygen flow) and the special procedure (with additional oxygen flow, dilution with o-xylene to the N-level of approx. 50mg/l etc.), is presented.

| Sample ID | Expected TN concentration | Recovery, % | |
|---|---|---|---|
| | | Common procedure | Special procedure |
| Residual fuel 1 | 0.64 % wt. | 73 | 95 |
| Residual fuel 2 | 0.136 % wt. | 97 | 101 |
| Residual fuel 3 | 0.7 % wt. | 71 | 97 |
| Residual fuel 4 | 0.68 % wt. | 73 | 95 |

*Table 1. Results of experiments used different procedures.*

## Alternative energy sources

World economies remain overwhelmingly based on hydrocarbons. According to the International Energy Agency, in 2010 hydrocarbons provided 81 percent of the world's energy. [4] All fossil fuels are non-renewable, and as such they will eventually be depleted. Additional and alternative sources for intermediate and final products, whether fuels or petrochemicals, contribute to the conservation of petroleum resources and provide additional raw material options for generating of the same products. [5] Examples of the alternative sources include corn fermentation for ethanol, BTX (benzene, toluene, and xylenes) from coal, biogas or bioliquid from agricultural wastes, jet fuel from shale oil or crop oil, liquid fuels from spent tires or mixed waste, etc. [5], [6]

Also residues from forest industry are used for the production of innovative biofuel. Raw wood oil material and made from it biodiesel samples were successfully investigated using multi EA® 5000 in order to estimate nitrogen content. In the table below the results are presented.

| Sample | TN content |
|---|---|
| Crude Tall Oil | 99.91 mg/kg |
| Biodiesel | 100 µg/l |

*Table 2. Results of TN content determination of crude tall oil and based on it biodiesel.*

There are many other sources for creating more advanced biofuels from wastes and residues. There is a high potential to produce fuels from used cooking oil, industrial waste, waste paper, food, wood, plant material. Creating more advanced biofuels from wastes and residues, which might otherwise be left to decompose, offers one opportunity to reduce the carbon-intensity of transport fuels without creating significant impacts on food commodity markets or land resources. [7]

## Summary

Control of nitrogen content in raw materials, intermediates and final products is one of the crucial issues during the refinery processes. Because of the rapid depletion of exhaustible fossil fuel resources, refinery processes increasingly dealing nowadays with heavy oil fractions. It was shown that the multi EA® 5000 performs successful work for investigation of such difficult matrices with high boiling points compounds and high nitrogen contents. The application of additional oxygen supply in the mixture with argon gas during the first step of combustion contributes to the complete digestion of the samples and provided reliable results.

Furthermore, the instrument was successfully applied for determination of nitrogen content in very promising and well growing field of alternative fuel sources.

## Sources

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