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Determination of total nitrogen content by different approaches in petroleum matrices

Antoaneta I. Pavlova [a,*], Dimitar S. Dobrev [b], Pavlina G. Ivanova [a]

[a] Analytical Methods Group, Research and Development Laboratory, LUKOIL NEFTOCHIM BOURGAS JSC, Bourgas 8104, Bulgaria
[b] Process Engineer Department, LUKOIL NEFTOCHIM BOURGAS JSC, Bourgas 8104, Bulgaria

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ABSTRACT

Two analytical methods are developed and validated for determination of low total nitrogen levels (below 0.0150%) in different petroleum matrices. The experimental and the instrumental conditions are optimized during the study. The oxidative combustion method with chemiluminescence's detection is automatic with less handling while the Kjeldahl method involves more manual handling procedures and hence, has more potential for problems rise from contamination. The oxidative combustion with chemiluminescence's detection method is more sensitive, faster (i.e. the determination requires few minutes compared to several hours with Kjeldahl method) and lees hazardous (i.e. no handling of dangerous boiling sulfuric acid). The estimated analytical characteristics suggest that two methods are reliable: the mean values of recovery for the Kjeldahl method and the other method are respectively 91.5% and 98.6%. The relative uncertainties are less than 2.5% and 2.8% respectively for the developed methods. The detection limits, based on the triple standard deviation, are 5 and 0.03 mgN kg^{-1} respectively.

1. Introduction

It is well known that heterocyclic compounds containing nitrogen and sulfur are involved in chemical processes of fuel instability. Present knowledge suggests that for some fuels, the nitrogen content can be the main reason for the formation of insoluble sediments and gums under conditions of ambient and accelerated storage.

Many nitrogen compounds can poison refinery catalysts. They tend to be the most difficult class of compounds for hydrogenation, so the nitrogen content remained in the product of a hydrotreator is a measure of the hydrotreating process effectiveness. Some process catalysts used in petroleum and chemical refining can be poisoned even if the feeds contain only traces of nitrogen.

Most of the techniques for detail analysis of nitrogen compounds in petroleum matrices use gas chromatography equipment with different detectors or gas chromatography-mass spectrometry [1–7]. However, for monitoring purposes or routine analysis the determination of total nitrogen is preferred as it provides more information about the technology processes under study.

The well-known Kjeldahl method is a primary method for determination of total nitrogen in lubricating oils and fuels. An American Society for Testing and Materials (ASTM) method is established for the analysis of total nitrogen in lubricating oils and fuels by modified Kjeldahl method [8]. The first step for the total nitrogen determination is the sample digestion in order to convert organic nitrogen compounds into inorganic form mainly nitrate, nitrite or ammonium. Concerning to mineralization, it is the most tedious and time consuming step and at the same time the greatest source of analytical determination errors. Especially, the problems rise as this method is applied for determination of total nitrogen below 0.0150% wt. The recent developments in Kjeldahl method nitrogen determination are focused mainly in automation of the digestion procedure.

An alternative of the Kjeldahl method is oxidative combustion and chemiluminescence detection method for the petroleum products nitrogen content determination [9–11]. In general, chemiluminescence detection is gaining popularity and it offers advantages over other optical techniques [12]. The chemiluminescence's response, together with the background current, places these detectors among the most sensitive analytical instruments. Because of the unique chemistry of each chemiluminescence's reaction, the detectors are inherently very selective. These characteristics make it possible to detect very small amounts of desired compounds in the complex matrices. In addition, good repeatability and accuracy of the chemiluminescence technique makes it a viable tool for routine analysis.

Based on the industrial needs, our work consists of nitrogen content quantitative assessment establishment of various petroleum matrices by using different approaches. This study involves an application of two test methods of total nitrogen content determination

* Corresponding author. Tel.: +359 5511 2261; fax: +359 5511 5555.
E-mail address: Pavlova.Antoaneta.I@neftochim.bg (A.I. Pavlova).

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in petroleum matrices according to the nitrogen concentration. In order to improve the methods characteristics the modifications of procedure steps are experimented.

2. Experimental

2.1. Kjeldahl method

The apparatus B?CHI Digestion unit K-424, B?CHI Distillation unit K-324 (B?CHI Switzerland) and UV/VIS Spectrometer model Lambda 17 (Perkin Elmer, USA) are used for determination of total nitrogen content by Kjeldahl method.

UV/VIS Spectrometer (190–900 nm) equipped with glass cell of 20 mm optical path length is used for measurement of absorbance at 440 nm.

The reagent grade chemicals (purity > 99.9%) are obtained from Merck KGaA (Darmstadt, Germany) and Sigma-Aldrich GmbH (Seelz, Germany). The used water is double distilled after deionization. Ammonium sulfate dissolved in water with a concentration of 100 μgN is used for stock standard solution. The diluted standards in the range of 5–100 μgN prepared from the stock standard solution are used for instrument calibration. A blank test in parallel with the determination using water in place of the sample is carried out to determine a blank value.

In order to establish linear of calibration graph an equation is calculated by computer. The equation of the line type $A = a + bC$ is received where A is the absorbance measure and C is the nitrogen concentration of μgN/10 mL. The equation constants a и b related to the ordinate intercept and the calibration graph slope correspond to $A = 0.015 + 0.0029C$, $r^2 = 0.9998$.

2.2. Oxidative combustion method with chemiluminescence's detection

Nitrogen Analyzer model Antek 9000 N (Antek Instruments, Inc., USA) is used for high temperature oxidative combustion of petroleum samples and quantitative determination of the total, chemically bounded nitrogen by chemiluminescence's detection. Argon, high-purity grade (99.998% purity) is used as carrier gas; oxygen, high-purity grade (99.75% purity) is used for oxi-combustion and ozone generation.

Nitrogen species in the sample is converted into nitric oxide. The furnace oxidative temperature is kept at 1050 °C. The nitric oxide reacts with ozone to produce an excited state of nitrogen dioxide (NO_2^*). When nitrogen dioxide (NO_2^*) decays to its ground state, it emits light. The light is measured with a chemiluminescence's detector that correlates to nitrogen amount in the sample.

Pyridine dissolved in isooctane with a concentration of 100 ngN μL^{-1} is used for stock standard solution. The diluted standards in the range of 1–100 ngN μL^{-1} are used to calibrate the apparatus. The system performance must be checked with the calibration standards at least once per day. The samples are introduced by direct injection of 8 μL in the quartz combustion tube. The optimal instrument parameters are shown in Table 1.

The certified organic standard, tri-element (ERT-037, Tekmar part number 511–945) containing pyridine 100 mgN kg^{-1} (as N) is obtained from Cerilliant Corporation, TX, USA and it is used for optimization of nitrogen detector selectivity.

Data acquisition, instrument operation and data management are handled by computer and by 32-bit Windows™ based software.

2.3. Samples of analyses

The test petroleum matrices used in this study are as follows: catalytical reforming unit feed; aromatic hydrocarbons-benzene and xylenes; light gasoline fraction, light diesel fraction obtained in crude oils atmospheric distillation unit; gasoline fraction, light diesel and middle diesel fractions produced from fluid catalytic cracking unit; light diesel and middle diesel fractions produced at hydrocracking unit of Lukoil Neftochim Bourgas JSC, Bulgaria.

Table 1
Instrument parameters of oxidative combustion method with chemiluminescence's detection

Parameters	Value
Cycle time	15 min
Baseline delay	10 s
Oxidative furnace	1050 °C
Inlet argon	140 mL min^{-1}
Inlet oxygen	25 mL min^{-1}
Pyro oxygen	450 mL min^{-1}
Nitrogen ozone	25 mL min^{-1}
Detector high voltage	810 V
Detector gain	High
Sensitivity	×25
Thermoelectric cooler	5 °C

3. Discussion

The Kjeldahl method is one of the oldest total nitrogen determination methods dating back to the last century and is a classical wet chemistry. This method coverts organic nitrogen to ammonia and requires sample digestion by strong acid followed by lengthy distillations.

The mineralization with sulfuric acid is a complex combination of oxidative, reductive and hydrolysis processes. However, the different nitrogen compounds (according to their chemical structures) undergoing change in different streams frequently lead to losses. Only the nitrogen from compounds with NH-functional group is converted in ammonium sulfate quantitatively. All the other types of nitrogen compounds (heterocyclic nitrogen, nitro-, and nitrozo-nitrogen) are digested difficulty and incompletely. The nitrogen, which is converted not completely in ammonium sulfate is separated as nitrogen element.

In order to evaluate the selectivity and the efficiency of the Kjeldahl method, different nitrogen compounds are selected and analyzed. The nitrogen species recovery is presented in Table 2. Pyridine and indole are digested and distillated difficult. A recovery efficiency of these compounds less than 85% is obtained. Acetamide, nitrobenzene, ethanolamine and aniline show higher recovery efficiency by Kjeldahl method in comparison with pyridine and indole. The total nitrogen recovery is about 91.5%.

The method usually involves high temperature (390 °C) digestion of the sample using concentrated sulfuric acid, various catalysts and salts to elevate the acid boiling point. A variety of sample amounts, catalyst dose are investigated to achieve complete matrix digestion. In order to determine the precision of digestion duration it is established that little amount of petroleum sample and sulfuric acid are necessary for fast mineralization.

Table 2
The nitrogen species recovery

Nitrogen species	Total nitrogen content in iso-octane, mgN kg^{-1}	Measure total nitrogen content, mgN kg^{-1} ($n = 6$)	Recovery, %
Aniline	101.8	98.8	97.1
Ethanolamine	108.3	106.3	98.2
Acetamide	100.0	96.7	96.7
Pyridine	123.8	95.3	76.9
Indole	121.7	103.8	85.3
Nitrobenzene	101.6	96.0	94.5