



## Development of a rapid and accurate method for the determination of sodium in vacuum gas oils (VGOs) by ICP-OES



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### ARTICLE INFO

#### Keywords:

Sodium  
VGO (vacuum gas oil)  
Dry ashing  
ICP-OES

### ABSTRACT

Sodium in vacuum gas oils (VGOs), even at trace levels, produces corrosion by-products in the refinery pipelines and it is a significant catalyst poison, especially for those from atmospheric or vacuum distillation units, thus its concentration in middle-distillate petroleum products needs to be controlled.

In addition, sodium contamination was an issue in this study, as sodium might be present even in the dust floating in the air. The use of an ultrapure sodium-free water and the disposal of a clean and dust-free room were the key to be successful on the development of this method.

Different sample preparation methods were studied as sample preparation optimisation was an important step in this study. Dry ashing by different processes, wet acid digestion with different acid mixtures, wet acid microwave-assisted digestion, and dilution with a proper solvent were tried to find the appropriate sample preparation method.

An accurate and precise method for the determination of sodium in vacuum gas oils (VGOs) by ICP-OES at trace levels has been developed by ashing the sample with a new piece of equipment designed and created by the Instituto de Tecnología Cerámica (ITC), that permits to calcine the sample in one hour and avoids analyte losses or analyte contamination. The quantification limit achieved by the whole sodium determination method is lower than  $1 \text{ mg kg}^{-1}$ , which allows it to be used as control method in the petrochemical industry.

### 1. Introduction

Sodium in middle-distillate petroleum products may cause important issues to the refinery plant, such as pipeline corrosion or catalyst poisoning problems in the conversion units. Crude oil formation is a difficult process that involves the decomposition of organic matter at high pressure and air absence into porous rocks. Duyck et al. [1] mentioned that metals in crude oil occur in different organic and inorganic forms, as it is a complex matrix containing mostly saturated and aromatic hydrocarbons, but also heteronuclear compounds, emulsified water and minerals. Therefore, these samples with complex matrices are difficult to analyse directly, and, besides, sample preparation methods are long and usually drive to contamination or analyte losses [2].

Thus, inorganic sodium salts are related to their formation process and they are dissolved in the water present in the oil deposits. Their presence is maleficent, even at trace level, as they can cause a lot of problems of dirtiness and poisoning. Excessive inorganic salt levels in middle-distillate petroleum products lead to pipeline corrosion problems, such as pipelines obstruction with corrosion by-products due to

the salts hydrolysis, which bring about acid formation, such as hydrochloric acid [2]. Metals, in their salt form, can contaminate distillate fractions and produce a decrease in their stability or a bad operation of the engines that use them as combustible. Sodium, or its salt form, such as sodium vanadate, usually accumulates in vacuum and atmospheric distillation towers and promote the weathering in these units, as they decrease the refractory melting point [3].

Furthermore, the presence of different species of metals in the refinery conversion units takes to catalyst poisoning. Most of the catalysts used in the refinery are porous to offer a proper contact surface to ease the posterior reactions and increase their yield. A catalyst poison can be defined as any substance that changes the physical or chemical properties of the catalyst. Physical poisoning comes from the porous clogging with corrosion by-products. Consequently, even though the catalytic centre has not changed its activity, chemical compounds cannot access the catalytic active centre, so the yield of the conversion reaction is lower. Chemical poisoning comes from the reaction of some metals, such as sodium, with the catalytic active site so that it loses its catalytic activity as the poison stays chemically bonded to the catalyst [4]. Since sodium causes both types of catalytic poisoning, it must be controlled to

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prevent the deactivation of the catalyst. Therefore, it is important to find a method capable to measure the total sodium content managing the matrix issues, rapid and with a low detection limit.

Literature was checked and some standard methods were found. According to BS EN 241:2000, sodium can be analysed in liquid petroleum products by Atomic Absorption Spectrometry (AAS here in after). Samples are subjected to a carbonisation process with a Bunsen Burner and a subsequent calcination with a muffle furnace. Then the ashes are digested with hydrochloric acid and make up with ultrapure water.

Refining is a continuous process, so sodium determination has to be a quick measurement. Some middle distillate petroleum products are normally imported from other refineries. Consequently, the main problem with the standard method (BS EN 241:2000) arises when the vessels must wait to discharge the product while the sodium content, among other properties, is being checked, as this determination takes eight hours.

Sample dilution with an appropriate solvent would be the perfect method, as it would be just a single-step sample preparation method, being faster and less risk to get the sample contaminated or suffer analyte losses. Two standard methods give the possibility of measuring sodium in hydrocarbons with a single-step sample preparation method. ASTM D7111 and ASTM D5863 (Test Method B) explain how to measure some metals (sodium among them) by diluting the sample with a solvent and analysing by AAS or inductively coupled plasma optical emission spectrometry (ICP-OES here in after). However, even though ASTM D7111 offers an acceptable concentration range and detection limit for sodium, as well as a short analysis time, this standard method has only been applied to diesel and jet fuels. This means that samples with a more complex matrix such as vacuum gas oil have not been considered and they are more difficult to analyse due to their high viscosity. Additionally, for those samples that have solid particles, standards propose to filter the sample to eliminate them, not considering that maybe these particles might contain the analyte [5]. On the other hand, ASTM D5863 works with fuel oils, which have a more complicated matrix to handle than VGOs, but its concentration range is too high (1–20 mg kg<sup>-1</sup>), as the aim of this work is to achieve a quantification limit lower than 1 mg kg<sup>-1</sup> [6]. This standard method also explains another procedure (Test Method A) that implies the calcination of the sample and the subsequent digestion of the ashes. Nevertheless, this kind of sample preparation, as well as the one suggested by the standard method BS EN 241:2000 takes at least eight hours so, the test is too long [7].

Therefore, nowadays, there is not a method that satisfies the three requirements needed, which are quantifying the total sodium managing the matrix issues, having a quantification limit under 1 mg kg<sup>-1</sup> and carrying out the whole analysis process in less than 4 h.

Six sample preparation methods were studied, and they are classified in three categories depending on its theoretical fundamentals:

1. Direct measurement by diluting the sample with solvent
  - a. Direct measurement by diluting the sample with kerosene.
  - b. Direct measurement by creating a microemulsion with ethanol.
2. Wet acid digestion
  - a. Sample decomposition by wet acid digestion (heating and stirring).
  - b. Wet digestion assisted by microwave radiation.
3. Dry ashing
  - a. Dry ashing by Bunsen burner carbonisation and muffle furnace calcination.
  - b. Sample decomposition by dry ashing in a new piece of equipment designed and created by the Instituto de Tecnología Cerámica (ITC).

The aim of this study is to develop a rapid and accurate method for the determination of sodium in VGOs at trace levels, establishing an appropriate sample preparation method that overcomes the difficulties

of the sample matrix and comparing the accuracy, detection and quantification limits of ICP-OES or AAS, choosing the appropriate one.

## 2. Experimental

### 2.1. Instrumentation

An Agilent 5100 SVDV inductively coupled plasma atomic emission spectrometer equipped with a vertical torch with a 1.8 mm internal diameter injector, solvent resistant tubing, and a double pass cyclonic spray chamber was used for all the measurements. The instrument characteristics are described in previous works [8,9].

A Perkin Elmer AAnalyst 400 at. absorption spectrometer using a sodium hollow cathode lamp as light source was needed to perform the analysis.

A Mettler-Toledo model XS105 balance with a sensibility of 0.01 mg was used for preparing all the working standards and samples.

An UNITRONIC 200 thermostatic water bath and an ULTRASONICS ultrasonic bath, both from P-SELECTA, were required to homogenise sample's matrices.

An Anton-Paar microwave from Paar-Physica, with an eight-position rotor and quartz vessels, was used to digest the samples.

A N50 electric muffle furnace from Nabertherm capable to achieve a temperature of 1200 °C was used to calcine the samples.

A new furnace designed by ITC was developed in order to optimise a new carbonisation method based on a low-oxygen atmosphere and allowing the carbonisation of the sample in 1 h approximately.

### 2.2. Reagents and standards

All reagents were of the highest purity grade. The absence of emission peaks near the region of the emission line selected for Na (588.995 nm) evidences that the purity was satisfactory.

Reagents and standards used are listed in the following sections and classified depending on the type of the sample preparation method that were used.

#### 2.2.1. Direct measurement by diluting the sample with solvents

The organic calibration standards were prepared from a Conostan Mineral Oil Single-Element Standard, containing 1000 mg kg<sup>-1</sup> of Na (traceable to NIST SRM 1069b sodium cyclohexanebutyrate) while the validation standards were prepared from a Conostan Mineral Oil Multi-Element Standard S-21, containing 100 mg kg<sup>-1</sup> of Na.

Conostan Mineral Oil Single-Element Standard of 1000 mg kg<sup>-1</sup> of Y was used as internal standard.

A Conostan base oil free of analyte with a room temperature viscosity of 75 cSt was used for standard preparation to match the matrix of standards and hydrocarbon samples. This viscosity was chosen because it was the highest commercially available.

Kerosene supplied by Conostan and ethanol from Merck were used as diluents.

Triton X-100 from Merck was used as surfactant.

#### 2.2.2. Wet acid digestion

Nitric acid, hydrochloric acid and hydrogen peroxide from Merck were used to digest the samples in both methods, wet digestion and microwave-assisted acid digestion.

The aqueous calibration standards were prepared from a Merck Single Element Standard, containing 1000 mg L<sup>-1</sup> of Na (traceable to NIST SRM NaNO<sub>3</sub> in 5 mol/l of HNO<sub>3</sub> Certipur) while the validation standards were prepared from a Merck ICP multi-element solution V containing 1000 mg L<sup>-1</sup> (traceable to NIST SRM 3152a)

#### 2.2.3. Dry ashing

Hydrochloric acid from Merck was used to digest all the sample ashes. It was diluted with pure water (sodium-free) from Merck.

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