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

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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 $1 \, \mathrm{mg \, kg^{-1}}$, 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 loses. 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^{-1}), as the aim of this work is to achieve a quantification limit lower than 1 mg kg^{-1} [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^{-1} 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 ULTRASONS 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^{-1} 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^{-1} of Na.

Conostan Mineral Oil Single-Element Standard of 1000 mg kg^{-1} 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^{-1} of Na (traceable to NIST SRM NaNO$_3$ in 5 mol/l of HNO$_3$ Certipur) while the validation standards were prepared from a Merck ICP multi-element solution V containing 1000 mg L^{-1} (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.

Table 1

Density and viscosity sample values and the API number of the three VGO samples used in this study.

	Viscosity[a] (cSt)	Density[a] (kg m^{-3})	API number
VGO − 1	6.5	940	19.0
VGO − 2	5.0	930	20.7
VGO − 3	7.0	910	24.0

[a] All the densities are measured at 15 °C. Viscosities are measured at 100 °C.

The calibration and validation standards were prepared from the same standards than by Wet acid digestion methods.

2.3. Samples

Several vacuum gas oils with different physical properties were analysed. Table 1 shows density and viscosity sample values and their API number.

According to the American Petroleum Institute (API), liquid petroleum products are classified as light, medium or heavy depending on its API gravity degree. It is calculated from its Specific Gravity (SG), following Eqs. (1) and (2) [9]:

$$SG \; oil = \rho_{hydrocarbon}/\rho_{H_2O} \tag{1}$$

$$API \; gravity \; = \; 141.5/SG\text{-}131.5 \tag{2}$$

2.4. Avoiding contamination

Contamination is a serious problem in this study as sodium is one of the most abundant elements on Earth, so samples are really easy to contaminate if the sample preparation method is not careful enough.

The use of pure water (with sodium content less than $0.1 \, \text{mg L}^{-1}$) was necessary to dilute samples and to clean thoroughly the laboratory ware.

In addition, running the sample preparation in a clean room free of dust that could contain sodium, and the use of exclusive laboratory plasticware, just dedicated to sodium determination, will help to avoid contamination, and so, it will improve the detection and quantification limits.

Finally, all the solutions, both samples and standards, should be stored in HDPE plastic bottles.

2.5. Experimental procedure

2.5.1. Optimisation of sample preparation

Different sample preparation methods were studied to find the appropriate method to prepare the sample that allows to find the lowest quantification limit and permits to spend the least time and sources possible.

Prior to study the sample preparation methods, samples had to be heated and stirred at 60 °C during 30 min in a thermostatic and ultrasonic bath, to make them pourable and homogeneous.

The optimisation of the measurement conditions (power, nebuliser flow, pump rate, and read time) was carried out in order to obtain the best signal-noise ratio for the different sample preparation methods developed.

Following the same procedure established in two previous studies [8,9], the optimum working conditions for samples diluted with kerosene were:

Power – 1.5 kW, Nebuliser flow – $0.5 \, \text{L min}^{-1}$, Pump rate – 6 rpm, and Read time – 15 s.

Equally, the optimum working conditions for aqueous solutions were:

Power – 1.4 kW, Nebuliser flow – $0.7 \, \text{L min}^{-1}$, Pump rate – 10 rpm, and Read time – 7 s.

2.5.1.1. Direct measurement by diluting the sample with solvents

2.5.1.1.1. Direct measurement by diluting the sample with kerosene. ASTM D7111 [5] suggests the direct measurement by diluting the sample with a suitable solvent, as it is a single-pass sample preparation and it is rapid and easy. Therefore, kerosene and ethanol were used in order to find the appropriate one.

Sample dilution with kerosene and ethanol with 1:5 dilution ratio was tried as it is the simplest way to prepare the sample. Blank oil analyte-free with 75 cSt was introduced in the calibration and validation standards to match the sample viscosity.

The prepared solutions with kerosene as solvent were presenting solid particles so, they needed to be filtered before measuring them by ICP-OES. The solid particles were containing sodium thus, this method was discarded.

Sample dilutions prepared with ethanol as a solvent were not analysed as it was not possible to maintain stable and robust plasma conditions.

2.5.1.1.2. Direct measurement by creating a microemulsion with ethanol. The sample preparation method explained before did not work as expected. Consequently, another method without heating treatment was tried. As some literature suggests [1,2], VGO might still contain some inorganic salts in its composition so microemulsions with organic and inorganic standards were prepared to check that sodium from inorganic salts was being analysed too [10].

As organic and inorganic matrices are immiscible, Triton X-100 was used as surfactant to prepare a stable microemulsion, as Alexandre de Jesus et al. proposes in the literature [11]. The formula used was 8% (w/w) of nitric acid, 14.4% (w/w) of surfactant (Triton X-100), 20% (w/w) of sample and 57.6% (w/w) of ethanol. These microemulsions were introduced in the ICP-OES but they could not be analysed, as the plasma flame became unstable.

2.5.1.2. Wet acid digestion

2.5.1.2.1. Sample decomposition by wet acid digestion. Some authors such as Cortés et al. or Khuhawar et al. [12,13] suggested wet acid digestion to oxidise the organic matrix. Many acid mixtures and concentrations are proposed in the literature by many authors [13–15] so, in order to improve the method, these variables were optimised to get the minimum digestion time.

Table 2 shows the different acid mixtures and amount of sample tested to improve the digestion method.

The mixture of sample and acids were also submitted to a heating and stirring process at 100 °C for 24 h, adding more acid and hydrogen peroxide when needed, but none of them was digested after this time.

2.5.1.2.2. Wet digestion assisted by microwave radiation. The total digestion of liquid petroleum products by microwave radiation is also proposed in several reports [16–20]. Power, time and sample weight were optimised, as well as acid mixture concentration in order to achieve the total sample digestion in the minimum possible time (shown in Table 3)

The samples were not totally digested after running Methods 1 and 2, so power was risen to 850 W. Methods 3 and 4 were apparently digesting the samples but, when the solutions were made up to 100 ml

Table 2

Different acid mixtures and concentration ratios used in wet acid digestion.

Method	Sample weight (g)	Acid mixture and concentration	V (ml)
Method 1	4.00	HNO_3 (1:1)	25
Method 2	4.00	HNO_3 (conc)	20
Method 3	4.00	HCl (1:1)	30
Method 4	4.00	HCl (conc)	25
Method 5	4.00	HNO_3 (conc) + HCl (conc) Ratio (3:1)	25
Method 6	0.30	HNO_3 (conc) + H_2O_2 (30%) Ratio (3:1)	8

Table 3
Method conditions optimised in microwave assisted acid digestion.

Method	Sample weight (mg)	Time (min)	Max power (W)	Acid mixture and concentration
Method 1	100	35	800	2 ml HNO3 (1:1)
Method 2	200	45	800	5 ml HNO3 (1:1)
Method 3	200	35	850	5 ml HNO3 (conc)
Method 4	100	30	1000	3 ml HNO3 (conc) + 1 ml HCl (conc)
Method 5	200	35	1000	5 ml HNO3 (conc) + 1 ml HCl (conc)
Method 6	**100**	**35**	**1000**	**5 ml HNO3 (conc) + 1 ml HCl (conc)**

with water, two phases appeared not being completely digested.

Method 5 was not finishing the cycle as the pressure into the quartz vessels was too high. Thus, microwave equipment was stopping the digestion process as a security measure. This pressure problem was solved by reducing the sample weight to 100 mg and setting up the three steps of the Method 6 with the following characteristics:

Step 1: Power (W): 100–500; for 10 min
Step 2: Power (W): 1000–1000; for 10 min
Step 3: Power (W): 1000–0; for 15 min

Conditions used in Method 6 were chosen as the most suitable to reach the total digestion of this kind of samples.

After digesting the sample, it was transferred to a one-mark volumetric flask and the microwave containers were carefully cleansed and the solution was made up to 50 ml. The sample digestion was completed by Method 6, but the maximum amount of sample that permits running the method was too small. Consequently, it was suspected that the method was presenting a quantification limit too high to analyse samples with low sodium concentration.

2.5.1.3. Dry ashing

2.5.1.3.1. Dry ashing by Bunsen burner carbonisation and muffle furnace calcination. Dry ashing in accordance with Standard BS EN 241:2000 was studied. The principle of the method is the following. The sample is burnt in a platinum crucible and the carbon residue incinerated in a muffle furnace at 550 °C. The residue is taken up with ultrapure water and the sodium content of the aqueous solution is determined by means of AAS at a wavelength of 589.0 nm.

According to this standard, prior to the incineration of the sample in the muffle furnace, it has to be carbonised with a Bunsen Burner, trying to avoid a flame creation during the process, as it is extremely dangerous, requiring the constant awareness of the analyst.

Carbonisation was carried out by a Bunsen Burner in a crucible for two hours and the subsequent calcination in a muffle furnace for six hours at 1100 °C. After this treatment, ashes were digested in hydrochloric acid and heat for 30 min. Carbonisation and calcination time was tried to shorten by reducing sample weight and increasing temperature rate, but the results obtained were not successful, so it was concluded that sample preparation time could not be reduced.

To optimise the sample preparation method, nickel and platinum crucibles were tested, as nickel crucibles are much cheaper than platinum ones. After testing the method with both crucible materials, it was found out that nickel crucibles were flaked with the heat and acid mixtures during the process. The main problem was that the solution obtained had to be filtered to separate the degraded parts of the nickel crucible from the sample solution before measuring it by AAS or ICP-OES. It was noticed that this step was leading to sodium contamination, as well as, spectral interferences due to the high nickel concentration from the crucible.

In conclusion, the sample preparation process was taking too long to

consider it an appropriate method to control sodium in VGOs. Nevertheless, the optimisation of the method led to the conclusion that platinum crucibles were a better choice than nickel ones to perform calcination processes.

2.5.1.3.2. Sample decomposition by dry ashing in a new piece of equipment (designed and assembled by ITC). A new sample calcination prototype was built in ITC inspired in Williams et al. studies [21]. The prototype was designed with a small furnace cavity which permitted a faster temperature increase preventing the formation of a flame inside the platinum crucible, that would lead to analyte losses.

Different materials, capacity and shapes of the furnace were studied and, finally, the optimum conditions were found.

Fig. 1 in the Supplementary Material shows the furnace and the platinum crucible where the sample was introduced. The furnace measures are also shown. All the furnace material parts were sodium-free in order to avoid contamination, and the crucible was closed with a platinum cap.

Different heating cycles were studied in order to adapt the calcination heating cycle to the matrix sample. The purpose was to find the shortest cycle that allowed the calcination of the whole organic matrix. The optimal heating cycle was the following: 10 min to 110 °C, 10 min to 250 °C, 10 min to 500 °C and 30 min to 750 °C.

The whole calcination process was reduced to 1 h, 6 h less than the time necessary to calcine the sample following the BS EN 241:2000 dry ashing method.

Some calcination tests were run with different sample weight varying between 1 and 5 g to optimise the amount of sample. It was found that 2 g was the maximum amount of sample that was properly calcined with this short heating cycle, which was much more than the maximum amount of sample of the microwave method.

Once the sample was calcined, the ashes were digested introducing in the crucible 5 ml of hydrochloric acid (1:1) and sodium-free water until its rim and heating the crucible for 20 min. It was important to keep the crucible closed with the platinum cap so as to avoid contamination or analyte loses, due to the boiling process. Then, it was poured in a polypropylene one-mark flask and made up to 50 ml. The solutions were stored in HDPE bottles.

As there are not certified reference materials commercially available, samples were also spiked with a sodium organometallic standard solution prior to the calcination process. 0.50 and 1.00 mg kg^{-1} of Na spiked samples were also subjected to the whole analysis process in order to assess the accuracy of the method.

2.6. Calibration

Calibration standards were prepared according to the sample preparation method used. Six sample preparation methods were studied but only two of them were working.

2.6.1. Wet digestion assisted by microwave radiation

Four calibration standards of 0.01, 0.02, 0.05 and 0.1 mg kg^{-1} of Na were prepared by appropriate stepwise dilution of the inorganic standard of 1000 mg kg^{-1} of Na.

5 ml of concentrate nitric acid (HNO$_3$) and 1 ml of concentrate hydrochloric acid (HCl) were added to the standards to match with sample solution matrices.

2.6.2. Sample decomposition by dry ashing in a new piece of equipment (designed and assembled by ITC)

Four calibration standards of 0.10, 0.20, 0.50 and 1.00 mg kg^{-1} of Na were prepared by appropriate stepwise dilution of the inorganic standard of 1000 mg kg^{-1} of Na.

5 ml of hydrochloric acid (1:1) were added to the calibration standards in order to match with sample solution matrices.

2.7. Validation

As no reference materials are commercially available, alternative methodologies were used to validate the developed procedure. It was validated by measuring different reagents (organic and inorganic, depending on the method) with a known and certified sodium content and the recovery calculated.

The method recovery (R) was calculated using Eq. (3).

$$R = C_{obs}/C_{RM} \qquad (3)$$

Where C_{obs} is the sodium concentration of the organic reagent when measured (mg·kg^{-1}), and C_{RM} is the known concentration of sodium of the reagent obtained from the certificate of analysis.

In this study, it has been chosen as accurate measurements those with a recovery range between 90% and 110%. Some other authors, such as Zhou and Wang [22], have considered a recovery range from 80% to 120%.

3. Results and discussion

In summary, direct measurement by diluting the sample with kerosene was not chosen as an appropriate method to analyse sodium concentrations because the need of filtering the sample brought about analyte loses. Microemulsions with ethanol did not work either since it was not possible to measure them by ICP-OES as the plasma flame was not robust enough. Wet acid digestion did not work properly for these kind of samples as they were not completely digested, even after 24 h of treatment. Finally, dry ashing sample preparation by the standard method BS EN 241:2000 was too long to be considered as a quality control test.

There were only two methods of sample preparation that could prepare the sample in less than 2 h and make the resulting solutions completely suitable for its analysis by ICP-OES. These methods were the wet acid digestion assisted by microwave radiation and the dry ashing method using the new piece of equipment designed and assembled by ITC.

VGOs sodium concentration was not known so, to conclude if the procedure developed was measuring the sodium concentration properly, 0.5 and 1.0 mg kg^{-1} spiked samples were analysed with the original sample and the results obtained were compared.

3.1. Wet digestion assisted by microwave radiation

Table 4 in the Supplementary Material shows the results obtained in the determination of sodium by wet digestion assisted by microwave radiation and measured by ICP-OES in the three samples studied: VGO-1, VGO-2 and VGO-3 with their corresponding standard additions of 0.5 and 1.0 mg kg^{-1}.

First column presents the value obtained by ICP-OES after measuring the prepared solutions. Second column shows the sample sodium concentration calculated considering the dilution ratio and third column indicates sample sodium concentration. Recovery value was calculated following Eq. (3).

As it can be seen in this table, the calculated recovery values are outside the range taken as acceptable, being this method discarded as a control method for the determination of sodium in VGOs by ICP-OES.

3.2. Sample decomposition by dry ashing in a new piece of equipment (designed and assembled by ITC)

Table 5 in the Supplementary Material shows the results obtained in the determination of sodium by ICP-OES after the sample calcination by dry ashing with the new furnace designed by ITC of three VGO samples. The first column presents the value obtained by ICP-OES after measuring the prepared solutions. Second column shows the sodium concentration present in the sample calculated considering the dilution

ratio. Recovery value was calculated following Eq. (3).

As it can be seen, the results obtained on the determination of sodium in VGOs by dry ashing in the new piece of equipment and measuring them by ICP-OES were satisfactory, as spiked samples were measured properly and the calculated recovery factors were between the desired range in all the analysed samples, that is 90–110%.

In addition, the method developed is also robust as VGOs with different properties, such as viscosity, density and sodium concentration were measured.

3.3. Calculation of the detection limit (L_D) and quantification limit (L_Q)

ICP-OES and AAS were chosen in this work as spectrometric techniques. As it is known, ICP-OES was prefered by its accuracy and precision, while AAS was selected for its simplicity of operation and low cost. Detection and quantification limit of the spectrometric techniques were calculated to choose which technique provided the quantification limit required.

The detection limit (L_D) and quantification limit (L_Q) were calculated from the measurement of a sample with a concentration 0.5 times the concentration of the lowest standard in the calibration curve. The sample was measured ten times under reproducibility conditions. The detection and quantification limit were obtained in accordance with the International Union of Pure and Applied Chemistry (IUPAC) guidelines from the following expression [8]:

$$L_D = 3.29 \cdot s \qquad (4)$$

$$L_Q = 10 \cdot s \qquad (5)$$

where:

s = value of the standard deviation of the measurements.

The detection limit obtained for ICP-OES was 0.002 mg kg^{-1} while the one for AAS was 0.010 mg kg^{-1}. As it is known, AAS detection limit is significantly higher than ICP-OES one, and it was not low enough to reach to the desired limits of the study.

An organic validation standard of 1 mg kg^{-1} of sodium was prepared with kerosene. This standard was subjected to both preparation methods developed, and then the both solutions obtained, were measured under reproducibility conditions by ICP-OES.

The results obtained by ICP-OES were calculated applying the dilution factor and the average and the standard deviation of the results were calculated. Following Eqs. (4) and (5), detection and quantification limit of the method were calculated, as it is shown in Table 6 in the Supplementary Material.

Microwave-assisted acid digestion had the highest quantification limit. It was not possible to reduce it, as sample weight had to be increased or final volume had to be reduced. An increment of the sample weight leads to higher pressure into the microwave containers, which is dangerous so, the microwave oven stops the digestion method as safety measure, which means that the digestion process is not completed. On the other hand, the reduction of the final volume can lead to analyte losses since a thorough cleaning of the sample containers involves a large amount of water.

Dry ashing with the new piece of equipment was chosen as the best method to determine sodium in VGOs because, even though the sample preparation method was taking more time than the digestion by microwave oven, its quantification limit was significantly lower than the one achieved by the microwave-assisted acid digestion and the total analysis time was still satisfying the aims of the study.

4. Conclusions

1. The developed method is rapid, accurate and has a quantification limit lower than 1 mg kg^{-1}.

2. The development of a sample preparation piece of equipment designed and assembled by ITC based on dry ashing of the sample has allowed the performance of the analysis in 1 h and 45 min approximately.

3. The point of the new piece of equipment to be so effective is the capability of increasing the temperature quickly avoiding analyte loses and sample contamination.

4. The handling of exclusive plastic material with an exhaustive cleaning led to lower detection and quantification limits than other methods found in the literature.

5. The new method developed by ITC is environmentally friendly, as its calcination process is significantly less time-consuming, so it reduces considerably the electric energy used in this process. In addition, as the organic matrix is decomposed, no hazardous organic waste is generated.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2018.06.015.

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