JAAS

Journal of Analytical Atomic Spectrometry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. García, M. Á. Aguirre Pastor and A. Canals, *J. Anal. At. Spectrom.*, 2019, DOI: 10.1039/C9JA00255C.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

New multinebulizer for spectrochemical analysis: wear metals determination in used lubricating oils by on-line Standard Dilution Analysis (SDA) using Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES)†

Miriam García, Miguel Ángel Aguirre* and Antonio Canals*

¹Department of Analytical Chemistry and Food Science and University Institute of Materials, Faculty of Science, University of Alicante, P.O. Box 99, 03080 Alicante, Spain

†Electronic supplementary information (ESI) available: Further experimental results.

*Corresponding authors: aguirre.pastor@ua.es (M.A. Aguirre) and a.canals@ua.es (A. Canals).

Abstract

A new multinebulizer has been employed for wear metal (e.g., Cd, Cr, Cu, Fe, Mn, Ni, Pb) determination in used lubricating oils. To this end, a multinebulizer-based analytical methodology has been proposed by on-line standard dilution analysis (on-line SDA) before inductively coupled plasma optical emission spectrometry (ICP OES) detection (multinebulizer/SDA/ICP OES), which is able to overcome typical limitations related with organic samples analysis in ICP-based techniques. This is accomplished by the simultaneous introduction of organic samples and aqueous calibration standards, keeping a minimal sample pretreatment (*i.e.*, dilution). The multinebulizer/SDA/ICP OES combination allows the determination of Cd, Cr, Cu, Fe, Mn, Ni and Pb in used lubricating oils with a limit of detection of 20, 10, 6, 20, 4, 30 and 200 ng g⁻¹, respectively. The subsequent analysis of spiked commercial lubricating oil samples has led to recovery values which range from 91 to 108 %. The efficiency of the proposed methodology has been checked by comparing its results with values obtained with conventional standard additions calibration and both limits of detection and recovery values were of the same order of magnitude. The proposed analytical methodology has the main advantage of ease of operation, as time and cost of analysis are reduced and the use of organic calibration standards is also avoided. Hence, the synergistic association multinebulizer/SDA is a simple, fast, relatively economic, environmentally friendly, direct and reliable way of wear metal monitoring in used lubricating oils by ICP OES.

1. Introduction

View Article Online
DOI: 10.1039/C9JA00255C

Engine components undergo continual wear under normal operating conditions, which is minimized by the use of lubricating oils. There may be physical wear which generates metallic particles due to friction, high temperature and pressure but also chemical wear may exist producing organometallic species. Despite the presence of filters and collectors, most of the wear metals remain in the lubricating oil and they are transported through the whole system.¹

Therefore, an increment in the concentration of several key elements in the lubricating oil after a period of activity may indicate some potential problems in components of the engine and their extent. Each element is related to a specific engine component and so a diagnosis of its state could be done based on elemental analysis of used lubricating oils. For example, an unexpected increase of Ni or Cr indicates corrosion in bearings or pistons, respectively. Another example less specific is the concentration of Fe that indicates corrosion in various parts of the engine.¹

Nowadays, elemental analysis of used lubricating oils is routinely performed for preventive maintenance, aimed at reducing any potential damage in the engine before irreversible damage occurs. Thus, this analysis brings economic benefits, reduces potential risks and helps in developing new maintenance procedures.

In order to obtain accurate results in this elemental analysis, sensitive techniques are required, since the capability of monitoring small concentration changes in key elements is needed. To date, most analytical techniques reported for this purpose are based on spectrometric techniques, such as Flame Atomic Absorption Spectrometry (FAAS),^{2–6} Electrothermal Atomic Absorption

1 Spectrometry (ETAAS),⁷ X-Ray Fluorescence Spectrometry (XRF),⁸ Laser
2 Induced Breakdown Spectrometry (LIBS),⁹ Inductively Coupled Plasma Optical
3 Emission Spectrometry (ICP OES),^{4,6,10–13} and Inductively Coupled Plasma Mass
4 Spectrometry (ICP-MS).¹ Traditionally, FAAS was extensively used due to its
5 lower cost and robustness. However, it is limited due to its low sensitivity and its
6 mono-elemental characteristics.¹ In regards to ETAAS, few applications have
7 been reported, due to its mono-elemental detection and the low sample
8 throughput. ICP-MS applications are still restricted because there are much
9 carbon deposits on the instrument interface and pronounced effects of organics
10 in the ICP, as well as its higher acquisition and operation costs. Currently, ICP
11 OES is by far the most applied technique for analysis of lubricating oil, mainly
12 because of its high sensitivity and multi-elemental analysis capability. It is as well
13 the preferred technique for the analysis of lubricating oils.¹³

14 Nevertheless, the main limitation of lubricating oil analysis lies in its matrix
15 complexity. The organic nature of the sample itself generates matrix effects and
16 its high viscosity hampers the proper sample introduction into the ICP. Moreover,
17 the high organic solvent load and the formation of carbon deposits on different
18 places of the plasma torch (*i.e.*, injector and/or concentric tubes) impose serious
19 difficulties and practical problems. In order to overcome these limitations, most
20 analytical procedures for ICP OES analysis of this type of sample involve a
21 previous step of sample preparation, including acid digestion,^{2,10}
22 emulsification,^{5,7,12} or dilution of the sample with organic solvents.^{3,4,6,11,13} The
23 acid digestion is reagents and time-consuming, besides the risk of sample
24 contamination, volatile analyte losses or incomplete mineralization of the organic
25 matrix. The main drawback of emulsification consists in the stability of the

emulsion. It depends on the chemical conditions (*i.e.*, pH, characteristics and concentration of the emulsifier), and it affects the sensitivity and reproducibility of the ICP OES signal. Due to its simplicity, sample dilution with organic solvents is the most common and preferred method. However, it is widely known that direct introduction of organic material into the plasma is fraught with several drawbacks, mainly related to matrix effects.

There have been numerous studies striving to solve these disadvantages which have been extensively reviewed for crude oil samples.¹⁴ Most of them have been focused on the optimization of instrumental and operating parameters, pointing out (i) decreasing the sample uptake rate; (ii) increasing or decreasing the temperature inside the spray chamber; (iii) using membrane-based and thermal-based desolvation systems; (iv) the use of higher RF power, or (v) the addition of oxygen, among others.¹⁴ In previous studies^{15–18} it was demonstrated that matrix effects caused by organic matrices can be avoided by using a multinebulization based system. This system allows the simultaneous introduction of organic and aqueous solutions into the plasma, reducing carbon deposits on the torch concentric tubes and at the tip of the injector tube. This implies an important advantage over conventional liquid sample introduction systems since it does not require the continuous cleaning of torch or the use of additional components such as cooled spray chambers or an auxiliary oxygen supply. Recently, a novel multinebulizer has been developed which allows a high mixing efficiency between two liquids, miscible or immiscible, since the mixing takes place under turbulent conditions of high pressure at the tip of the nebulizer. This mixing process inside the nebulizer creates a new concept in nebulization and allows chemical reactions by means of aerosols mixing.

Among all the solutions above mentioned dealing with the optimization of instrumental and operating parameters, several researchers also recommend the use of calibration strategies to compensate for matrix effects caused by organic matrices, being internal standard (IS)¹⁹ and standard additions (SA)²⁰ the most commonly employed in oil analysis. However, both calibration methods show advantages and limitations that are well documented.

Standard dilution analysis (SDA) has been recently proposed, which simultaneously combines the advantages of the SA and IS methodologies.²¹ The SDA method has been successfully applied to a wide variety of samples.^{21–26} However, from our knowledge, the use of the SDA method in direct introduction of organic matrices has not been previously reported since a large number of drawbacks need to be overcome (e.g., carbon deposits, matrix effects, etc.). Hence, the combination of both multinebulizer and SDA method results in a synergetic association for organic samples analysis with minimal sample pretreatment.

Therefore, the main purpose of this study was to assess the feasibility of the combination of the new multinebulizer and the on-line SDA method for real-world sample applications. To this end, the analysis of wear metals in used lubricating oils by ICP OES has been investigated as analytical problem. The on-line SDA has been adapted for working with the proposed multinebulizer and, additionally, the method efficiency has also been checked by comparing the results obtained by means of on-line SDA and conventional SA calibration. Finally, Eco-Scale²⁷ metrics were used and a comparison was made between the proposed method and the one described in the ASTM D5185-18 standard¹³ (See E.S.I. †).

2. Experimental

View Article Online
DOI: 10.1039/C9JA00255C

2.1. Instrumentation

All measurements were performed with an inductively coupled plasma optical emission spectrometer (model 720-ES, Agilent Technologies, Melbourne, Australia) working in axially viewed plasma mode. Table 1 shows the optimum operating conditions. The operating conditions of ICP OES were optimized aiming at reaching simultaneously the maximum emission signal for all analytes. The number of replicates throughout the work were five unless otherwise noted. No instrument's automatic sampler was used throughout the work.

The nebulizer used in this study was a multinebulizer (MultiNeb®, Ingeniatics, Seville, Spain)²⁸ (Fig. 1) which incorporates two independent liquid inlets into a single nebulization body with a common nebulization gas inlet and a unique outlet orifice. The liquid streams are mixed at the tip into the nebulizer and the aerosol of the mixture of the liquids exits by the unique hole. This multinebulization device is an advanced version of another previous prototypes already described elsewhere.^{29,30} In fact, the new multinebulizer represents a significant improvement since it allows mixing two liquids in aerosol phase inside the nebulizer under high pressure. As a result, there is an increase in the mixing efficiency and in chemical reaction speed.

The liquid sample introduction system was composed by the mentioned multinebulizer device coupled to a 50 mL internal volume cyclonic-type spray chamber (model Tracy, Glass Expansion Ptr. Ltd, West Melbourne, Victoria, Australia) without any additional modification required as the multinebulizer is built on the right dimensions to allow the easy connection to any commercial spray chamber typically used in ICP OES instruments. Two different types of

1 peristaltic tubes were used depending on the liquid: (i) for organic solutions, a tube
2 compatible with most petroleum-based products (F-4040-A, id. 0.76 mm, Ismatec,
3 Switzerland) was employed; and (ii) for aqueous solutions, a Tygon® tube (R-3607,
4 id. 1.65 mm, Ismatec) was used.

5

6 **2.2. Samples and reagents**

7 Samples of lubricating oil were provided from different local car
8 workshops. An unused lubricating oil (*i.e.*, sample A) and used lubricating oils
9 (*i.e.*, samples B-D) were employed as real-world samples. Used lubricating oils
10 were drained from different car engines during a routine service at a garage after
11 usage at certain mileage (*i.e.*, 20,000 km). They were labelled and stored in
12 amber glass flasks at 4°C. All oil samples were gravimetrically diluted (1:10) with
13 petroleum ether (QP, Panreac, Barcelona, Spain. Boiling range: 190–250 °C) in
14 order to decrease their viscosity. A blank containing petroleum ether was also
15 prepared. In addition, in order to evaluate matrix effects produced by the sample
16 matrix, three spiked samples were prepared adding a known amount of the
17 analytes using Conostan standard solution (SCP Science, Baie D’Urfé, Canada).
18 Moreover, the results obtained for on-line SDA and conventional SA calibration
19 were compared. Six organic calibration standards of 0.2, 0.4, 0.6, 0.8, 1.0 and
20 5.0 µg g⁻¹ were prepared using Conostan standard solution (SCP Science). The
21 calibration standards were prepared in petroleum ether and the blank was also
22 prepared using this solvent.

23 *Calibration with aqueous standard:* an aqueous calibration standard containing 4
24 µg g⁻¹ of the analytes was prepared by appropriate dilution of a multielemental
25 Merck IV stock solution from Merck (Darmstadt, Germany) containing 1000 µg

g⁻¹ of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Y (*i.e.*, internal standard). The solvent used was 1% (w w⁻¹) HNO₃ in distilled deionized water (18 MΩ cm resistivity) and the blank was also prepared using this solvent.

Auxiliary organic calibration standard: when on-line SDA is applied (Fig. 2), organic sample and aqueous calibration standards are pumped at different flow rate (see section 2.1. above). Therefore, a mathematical correction is needed for the different transport efficiencies of the nebulized organic and aqueous solutions. In this work, the relative transport efficiency (*i.e.*, sensitivity of channel 3 divided by sensitivity of channel 1, see Fig. 2) was calculated prior the analysis and it was obtained by pumping an auxiliary organic calibration standard (*i.e.*, 4 μg g⁻¹) through one channel (*i.e.*, channel 1 in Fig. 2) while aspirating a blank aqueous standard (1% (w w⁻¹) HNO₃) through the other one (*i.e.*, channel 3). Analogously, a blank organic (*i.e.*, petroleum ether) was introduced through channel 1 while nebulizing an aqueous calibration standard (*i.e.*, 4 μg g⁻¹) through the channel 3. Channel 2 was not involved in this experimental part. For each emission line evaluated, the ratio between the sensitivity values obtained from the calibration graphs was calculated, and finally, the average from all emission lines analyzed (*i.e.*, relative transport efficiency) was used. The relative transport efficiency in this research was 1.69 ± 0.07 working under optimum conditions (*i.e.*, channel 1: 0.5 mL min⁻¹; channel 3: 2.0 mL min⁻¹) (Table 1). For more details, the mathematical correction has been already described elsewhere.¹⁵

2.3. The on-line SDA methodology

The conventional SDA requires the preparation of two analytical solutions (*e.g.*, A and B) for each sample. Solution A, containing 50% sample and 50%

standard is gradually mixed with solution B, which contains 50% sample and 50% blank. As the standard is diluted (keeping the same amount of sample), many calibration points are generated over the time.²¹ Whereas, the on-line SDA was performed using three channels of the peristaltic pump accompanying the instrument used. A scheme of the system is shown in Fig. 2. The channel 1 (flow rate: 0.5 mL min⁻¹) was used to introduce organic samples. The channel 2 (flow rate: 2.0 mL min⁻¹) was used to perform the continuous dilution of the aqueous standard with the aqueous blank. Finally, the channel 3 (flow rate: 2.0 mL min⁻¹) was employed to aspirate aqueous standard (*i.e.*, analytes and internal standard). Internal standard concentration was calculated at different points of the SDA region by linear interpolation of Y emission line intensities within the baseline (zero concentration) and steady state signal (known Y concentration). Additional details on the mathematical approach used for calculation of concentrations using SDA can be found elsewhere.²¹

Analysis using conventional SA calibration was employed for comparison. For both methods, concentration values are the result of only one analysis and the uncertainty values are the estimated standard deviations of the extrapolated concentration.

3. Results and discussion

3.1. On-line SDA calibration

In the proposed on-line SDA calibration method, both analyte and internal standard signals are continuously and simultaneously measured during all the analysis. Fig. 3 shows an on-line SDA signal profile for one of the analytes investigated in this study. Three steps were required to apply the on-line SDA

using the multinebulizer. First, the organic (channel 1) and the aqueous (channel 3) blanks were simultaneously nebulized in order to rinse the system (step 1). Then, the organic sample (channel 1) and the aqueous calibration standard (*i.e.*, analytes and internal standard) (channel 3) were simultaneously introduced, achieving a stable maximum plateau (step 2). Afterwards, the aqueous blank (channel 2) was added to the aqueous calibration standard with the same flow rate, which resulted in the continuous dilution of the aqueous standard, that was continuously aspirated by the nebulizer (step 3). Finally, when a stable minimum is obtained, blanks were introduced again (step 1) to rinse the system and ready it for the next run (Fig. 3). Plotting the signal ratio between analyte and internal standard versus the inverse of the internal standard concentration in the region of dilution (step 3), a calibration curve was obtained.²¹ Fig. 4 shows the calibration curve corresponding to the signal graph shown in Fig. 3. Similar plots were observed for the other analytes. As it can be seen in Fig. 4, this calibration methodology provides many calibration points with a unique standard solution, giving rise to calibration curves with a great linear correlation for all analytes simultaneously measured.

3.2. Limits of detection (LOD) and quantification (LOQ)

Table 2 shows the limits of detection (LOD) and quantification (LOQ) for determination of wear metals obtained using both calibration methodologies (*i.e.*, on-line SDA and conventional SA). According to Eurachem guidelines,³¹ LOD is calculated by most conventions to be the analyte concentration corresponding to the obtained standard deviation at low levels (*i.e.*, standard deviation of the equivalent concentration found for 10 replicates of the blank) multiplied by a

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

factor, k . The IUPAC default value for k is 3.³² LOQ is calculated analogously to the LOD. However, the IUPAC default value for k is 10.³² In the present study, the LOD values obtained using on-line SDA calibration were similar or slightly higher than those obtained with conventional S calibration. Unfortunately, the figures of merit are not comparable due to the fact that both calibration methodologies were carried out using different sample introduction systems and different liquid flow rates. For conventional SA, a different nebulizer (*i.e.*, OneNeb®) and a lower sample flow rate (*i.e.*, 0.25 mL min⁻¹) was employed since it was necessary to enhance the plasma stability (*i.e.*, thermal conditions). As it can be seen in Table 2, the LOD values obtained for both nebulizers are in the same order of magnitude. This is a compromise between the negative effects of organic solvents³³ and the positive effects of aqueous solutions.³⁴ Even though, the multinebulizer operates with a higher sample flow rate (*i.e.*, 0.5 mL min⁻¹) it must bear in mind that the organic sample is diluted with the introduction aqueous standard calibration, achieving similar LOD. However, the synergistic combination of the multinebulizer and the SDA calibration strategy provides LOQ values which are fit for purpose with remarkable advantages over conventional SA. For instance, every sample is analyzed in 5 minutes (*i.e.*, 300 seconds, see Fig. 3) by SDA, whereas using conventional SA each sample is analyzed in 10 minutes due to the low sample flow rate and the number of calibration standard (*i.e.*, six calibration standards and the blank), increasing the sample throughput and reducing the total analysis time. Other remarkable advantages are handling simplicity and significant reduction of reagent and sample consumption and number of solutions to be prepared.

3.3. Analysis of lubricating oil samples

The multinebulizer/SDA/ICP OES analytical method was applied for wear metal determination in commercial lubricating oil of car engine before and after usage at certain mileage (*i.e.*, approximately 20,000 km). As it can be seen in Table 3, the analytes concentrations found in sample A (*i.e.*, unused lubricating oil) were below the LOQ, with the exception of iron, while in sample B (*i.e.*, used lubricating oil) they were higher than those obtained in sample A for all analytes, except for cadmium. Even though Cd is present in several alloys of the engine components, it is possible that no components containing Cd were exposed to corrosion and therefore its concentration is below the LOQ. The higher concentration found in sample B, for the majority of analytes, confirms the change in the elemental composition of the lubricating oil after a certain usage, as it was explained in the introduction. According to the results from Table 3, the concentrations of wear metals have increased which indicates possible wear of a number of components such as piston rings, ball/roller bearings or gears. The results for the used lubricating oil were under the limit values when comparing them with some typical values found elsewhere.³⁵ In any case, limit values are difficult to establish since these elements have multiple sources and the wear metal content depends on how much the oil has been used. It is important to note that these general guides are used only as an easy orientation and should not be used alone as a basis to take actions. In fact, interpretations are usually based on trends, comparing with the initial analysis of an unused oil sample and

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

information provided from the component manufacturer, the oil supplier company and/or experienced analysts.

Recovery test was performed for three used lubricating oil samples (*i.e.*, samples B, C and D) in order to check matrix effects. To this end, samples B-D were spiked with approximately 4 $\mu\text{g g}^{-1}$ of all analytes using organometallic standards and their final concentrations were determined by on-line SDA and by SA as comparative calibration methodology. Table 4 shows the analytes concentrations found in samples B-D. In all cases, quantitative recoveries were obtained, with recovery values for wear metals ranging from 91-108 % for on-line SDA. Hence, there is no evidence of systematic errors in the proposed method.

From a practical point of view, it should be noted that the analysis of these samples using on-line SDA calibration with the multinebulizer just required a ten times sample dilution as sample preparation. In addition, the preparation of a series of organic standards for each sample was avoided and only two aqueous calibration standards were prepared (*i.e.*, blank and standard solutions) for all samples instead. Moreover, the formation of carbon deposits at the tip of the injector tube and the torch concentric tubes was not observed. On the opposite side, when conventional standard additions calibration was employed, an extensive cleaning of ICP components was required after each analysis. Furthermore, a ten times samples dilution and 18 organic calibration standards were prepared to analyze 3 samples, increasing the number of solutions to be prepared and the total time of analysis in comparison to that involved in the proposed method.

Journal of Analytical Atomic Spectrometry Accepted Manuscript

3.4. Application of the Eco-Scale

View Article Online
DOI: 10.1039/C9JA00255C

An interesting feature of a new analytical method to be evaluated is its greenness. In order to quantify the environmental character, the Eco-Scale is an attractive attempt.²⁷ The results and discussion about the application of the Eco-Scale are given in the E.S.I. †

4. Conclusions

In this study, it has been demonstrated that the new multinebulizer (MultiNeb®) is valid for on-line SDA of wear metals and additives in used lubricating oils by ICP OES. The proposed analytical methodology (*i.e.*, multinebulizer/SDA/ICP OES) provides significant advantages: (i) SDA simultaneously corrects for matrix effects (*i.e.*, systematic errors) and for fluctuations (*i.e.*, random errors) due to changes in instrumental parameters; (ii) significantly reduces the time of the analysis as a minimal sample pretreatment is needed (*i.e.*, dilution), only one standard solution is required per sample and there is no need of preparing mixtures; (iii) provides ease of operation, since the system setup is simple, robust and easy to handle (iv) lower organic solvent consumption, as only aqueous standards are used; (v) there are no carbon deposits on different places of the plasma torch (*e.g.*, injector and/or concentric tubes); and (vi) it can be adapted to many analytes and sample types. The automatization of the whole analytical process can also be easily implemented and it is currently under study in our laboratory.

All these features result in a promising, robust, reliable, environmentally friendly and economical methodology for the analysis of used lubricating oils/organic samples/real-world samples by ICP OES.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1 Its greenness has also been quantitatively demonstrated by the application
2 of the Eco-Scale and the subsequent score comparison with the score obtained
3 with the method described in the ASTM D5185-18 standard.

4 **Acknowledgments:** The authors would like to thank the Ministry of
5 Economy and Competitiveness of Spain (project no. CTQ2016-79991-R,
6 AEI/FEDER, UE) for the financial support, Agilent Technologies Inc. for the loan
7 of the ICP OES spectrometer, and Ingeniatics for the MultiNeb® provided.

8
9 **Compliance with ethical standards**

10 **Conflict of interest:** There are no conflicts to declare

References

View Article Online
DOI: 10.1039/C9JA00255C

- 1 R. Q. Aucélio, R. M. de Souza, R. C. de Campos, N. Miekeley and C. L. P.
2 da Silveira, The determination of trace metals in lubricating oils by atomic
3 spectrometry, *Spectrochim. Acta Part B*, 2007, **62**, 952–961.
- 4 E. J. Ekanem, J. A. Lori and S. A. Thomas, The determination of wear
5 metals in used lubricating oils by flame atomic absorption spectrometry
6 using sulphanilic acid as ashing agent, *Talanta*, 1997, **44**, 2103–2108.
- 7 W. Yawar, Determination of wear metals in lubricating oils by flame atomic
8 absorption spectrophotometry, *J. Anal. Chem.*, 2010, **65**, 489–491.
- 9 T. Kuokkanen, P. Perämäki, I. Välimäki and H. Rönkkömäki, Determination
10 of heavy metals in waste lubricating oils by Inductively Coupled Plasma–
11 Optical Emission Spectrometry, *Int. J. Environ. Anal. Chem.*, 2001, **81**, 89–
12 100.
- 13 I. M. Goncalves, M. Murillo and A. M. González, Determination of metals in
14 used lubricating oils by AAS using emulsified samples, *Talanta*, 1998, **47**,
15 1033–1042.
- 16 P. Vähäoja, I. Välimäki, K. Heino, P. Perämäki and T. Kuokkanen,
17 Determination of wear metals in lubrication oils: a comparison study of ICP–
18 OES and FAAS, *Anal. Sci.*, 2005, **21**, 1365–1369.
- 19 S. Carballo, J. Terán, R. M. Soto, A. Carlosena, J. M. Andrade and D.
20 Prada, Green approaches to determine metals in lubricating oils by
21 electrothermal atomic absorption spectrometry (ETAAS), *Microchem. J.*,
22 2013, **108**, 74–80.
- 23 M. Pouzar, T. Černohorský and A. Krejčová, Determination of metals in
24 lubricating oils by X-ray fluorescence spectrometry, *Talanta*, 2001, **54**,

- 1 829–835.
- 2
- 3
- 4
- 5
- 6 2 9 L. Zheng, F. Cao, J. Xiu, X. Bai, V. Motto-Ros, N. Gilon, H. Zeng and J. Yu,
- 7
- 8 3 On the performance of laser-induced breakdown spectroscopy for direct
- 9
- 10 4 determination of trace metals in lubricating oils, *Spectrochim. Acta Part B*,
- 11
- 12 5 2014, **99**, 1–8.
- 13
- 14
- 15 6 10 R. F. Lara, S. M. Azcarate, M. Á. Cantarelli, I. M. Orozco, M. E. Caroprese,
- 16
- 17 7 M. Savio and J. M. Camiña, Lubricant quality control: A chemometric
- 18
- 19 8 approach to assess wear engine in heavy machines, *Tribol. Int.*, 2015, **86**,
- 20
- 21 9 36–41.
- 22
- 23 10 11 D. Prokic-Vidojevic, Z. Zivkovic and O. Barac, Application of atomic
- 24
- 25 11 emission spectrometry in aviation piston engine abnormal wear prevention,
- 26
- 27 12 *Sci. Tech. Rev.*, 2017, **66**, 23–28.
- 28
- 29
- 30 13 12 R. M. Souza, C. L. P. da Silveira and R. Q. Aucélio, Determination of
- 31
- 32 14 refractory elements in used lubricating oil by ICP-OES employing
- 33
- 34 15 emulsified sample introduction and calibration with inorganic standards,
- 35
- 36 16 *Anal. Sci.*, 2004, **20**, 351–355.
- 37
- 38
- 39 17 13 ASTM International, D5185-18, Standard Test Method for multielement
- 40
- 41 18 determination of used and unused lubricating oils and base oils by
- 42
- 43 19 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES),
- 44
- 45 20 ASTM International, West Conshohocken, PA, 2018, www.astm.org (last
- 46
- 47 21 accessed July 2019).
- 48
- 49
- 50
- 51 22 14 P. A. Mello, J. S. F. Pereira, M. F. Mesko, J. S. Barin and E. M. M. Flores,
- 52
- 53 23 Sample preparation methods for subsequent determination of metals and
- 54
- 55 24 non-metals in crude oil—A review, *Anal. Chim. Acta*, 2012, **746**, 15–36.
- 56
- 57
- 58 25 15 M. A. Aguirre, N. Kovachev, M. Hidalgo and A. Canals, Analysis of biodiesel
- 59
- 60

- and oil samples by on-line calibration using a Flow Blurring® multinebulizer in ICP OES without oxygen addition, *J. Anal. At. Spectrom.*, 2012, **27**, 2102–2110.
- 16 F. D. Avila Orozco, N. Kovachev, M. A. Aguirre Pastor, C. E. Domini, B. S. Fernández Band and A. Canals Hernández, Analysis of metals and phosphorus in biodiesel B100 from different feedstock using a Flow Blurring® multinebulizer in inductively coupled plasma-optical emission spectrometry., *Anal. Chim. Acta*, 2014, **827**, 15–21.
- 17 M. García, M. A. Aguirre and A. Canals, Determination of As, Se, and Hg in fuel samples by in-chamber chemical vapor generation ICP OES using a Flow Blurring® multinebulizer, *Anal. Bioanal. Chem.*, 2017, **409**, 5481–5490.
- 18 J. A. V. A. Barros, M. A. Aguirre, N. Kovachev, A. Canals and J. A. Nóbrega, Vortex-assisted dispersive liquid-liquid microextraction for the determination of molybdenum in plants by inductively coupled plasma optical emission spectrometry, *Anal. Methods*, 2016, **8**, 810–815.
- 19 S. L. dos Anjos, J. C. Alves, S. A. Rocha Soares, R. G. O. Araujo, O. M. C. de Oliveira, A. F. S. Queiroz and S. L. C. Ferreira, Multivariate optimization of a procedure employing microwave-assisted digestion for the determination of nickel and vanadium in crude oil by ICP OES, *Talanta*, 2018, **178**, 842–846.
- 20 A. P. Packer, J. E. S. Sarkis, M. F. Giné and É. J. dos Santos, High Pressure Asher (HPA-S) decomposition of biodiesel samples for elemental analysis by inductively coupled plasma optical emission spectrometry (ICP OES), *J. Braz. Chem. Soc.*, 2014, **25**, 743–749.

- 1
2
3 1 21 W. B. Jones, G. L. Donati, C. P. Calloway and B. T. Jones, Standard dilution analysis, *Anal. Chem.*, 2015, **87**, 2321–2327. View Article Online
DOI: 10.1039/C9JA00255C
- 4
5
6 2
7
8 3 22 D. A. Goncalves, T. McSweeney, M. C. Santos, B. T. Jones and G. L.
9
10 4 Donati, Standard dilution analysis of beverages by microwave-induced
11
12 5 plasma optical emission spectrometry, *Anal. Chim. Acta*, 2016, **909**, 24–
13
14 6 29.
- 15
16 7 23 A. Virgilio, D. Schiavo, J. A. Nóbrega and G. L. Donati, Evaluation of
17
18 8 standard dilution analysis (SDA) of beverages and foodstuffs by ICP OES,
19
20 9 *J. Anal. At. Spectrom.*, 2016, **31**, 1216–1222.
- 21
22
23 10 24 F. M. Fortunato, M. A. Bechlin, J. A. Gomes Neto, A. Virgilio, G. L. Donati
24
25 11 and B. T. Jones, Standard dilution analysis in flow system: Sodium
26
27 12 determination by flame atomic emission spectrometry, *Microchem. J.*,
28
29 13 2016, **124**, 662–667.
- 30
31
32 14 25 A. Virgilio, D. Schiavo, L. M. Costa, J. A. Nóbrega, B. T. Jones and G. L.
33
34 15 Donati, Inductively coupled plasma mass spectrometry and standard
35
36 16 dilution analysis applied to concentrated acids, *Talanta*, 2016, **161**, 826–
37
38 17 829.
- 39
40
41 18 26 F. M. Fortunato, A. L. Vieira, J. A. Gomes Neto, G. L. Donati and B. T.
42
43 19 Jones, Expanding the potentialities of standard dilution analysis:
44
45 20 Determination of ethanol in gasoline by Raman spectroscopy, *Microchem.*
46
47 21 *J.*, 2017, **133**, 76–80.
- 48
49
50 22 27 A. Gałuszka, P. Konieczka and Z. M. Migaszewski, Analytical eco-scale for
51
52 23 assessing the greenness of analytical procedures, *Trends Anal. Chem.*,
53
54 24 2012, **37**, 61–72.
- 55
56
57 25 28 Multineb®, <http://www.ingeniatrix.com/quimica-analitica/>, (last accessed
58
59
60

July 2019).

- 29 N. Kovachev, B. Almagro, M. A. Aguirre, M. Hidalgo, A. M. Gañán-Calvo
and A. Canals, Development and characterization of a Flow Focusing multi
nebulization system for sample introduction in ICP-based spectrometric
techniques, *J. Anal. At. Spectrom.*, 2009, **24**, 1213–1221.
- 30 M. A. Aguirre, N. Kovachev, B. Almagro, M. Hidalgo and A. Canals,
Compensation for matrix effects on ICP-OES by on-line calibration
methods using a new multi-nebulizer based on Flow Blurring® technology,
J. Anal. At. Spectrom., 2010, **25**, 1724.
- 31 B. Magnusson and U. Örnemark, Eurachem Guide: The fitness for purpose
of analytical methods – A laboratory guide to method validation and related
topics, (2nd ed. 2014). ISBN 978-91-87461-59-0. Available from
<http://www.eurachem.org> (last accessed July 2019).
- 32 L. A. Currie, Nomenclature in evaluation of analytical methods including
detection and quantification capabilities, *Pure Appl. Chem.*, 1995, **67**,
1699–1723.
- 33 A. W. Boorn and R. F. Browner, Effects of organic solvents in inductively
coupled plasma atomic emission spectrometry, *Anal. Chem.*, 1982, **54**,
1402–1410.
- 34 S. E. Long and R. F. Browner, Influence of water on conditions in the
inductively coupled argon plasma, *Spectrochim. Acta Part B*, 1988, **43**,
1461–1471.
- 35 Limit values from Oelcheck, https://en.oelcheck.com/wiki/Limit_values,
(last accessed July 2019).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

Figure captions

- Figure 1.** Side view (left) and front view (right) of the multinebulizer.
- Figure 2.** Scheme of the proposed on-line SDA using the multinebulizer.
- Figure 3.** On-line SDA signal profile in the determination of Fe in samples with organic matrix.
- Figure 4.** On-line SDA calibration curve for determination of Fe in samples with organic matrix.

Figure 1. Side view (left) and front view (right) of the multinebulizer.

Figure 2. Scheme of the proposed on-line SDA using the multinebulizer.

Journal of Analytical Atomic Spectrometry Accepted Manuscript

Figure 3. On-line SDA signal profile in the determination of Fe in samples with organic matrix.

Figure 4. On-line SDA calibration curve for determination of Fe in samples with organic matrix.

Journal of Analytical Atomic Spectrometry Accepted Manuscript

1 **Table 1.** Operating conditions.View Article Online
DOI: 10.1039/C9JA00255C

Parameter	Value
Radiofrequency power (kW)	1.20
Plasma gas flow rate (L min ⁻¹)	15
Auxiliary gas flow rate (L min ⁻¹)	1.5
Nebulizing gas flow rate (L min ⁻¹)	0.7
Number of replicates	5
Replicate read time (s)	1
Total liquid uptake rate (mL min ⁻¹)	2.5
Organic solution uptake rate (mL min ⁻¹)	0.5
Aqueous solution uptake rate (mL min ⁻¹)	2.0
Blank solution uptake rate (mL min ⁻¹)	2.0
Nebulizer type	MultiNeb®
Spray chamber	Cyclonic spray chamber
ICP Torch	Quartz with 1.4 mm i.d. injector
<i>Emission lines measured (nm)^a</i>	
Analytes	Cd II (214.439)
	Cr II (267.716)
	Cu I (327.395)
	Fe II (238.204)
	Mn II (257.610)
	Ni II (231.604)
	Pb II (220.353)
Internal standard	Y II (371.029)

2 ^a I: Atomic line; II: Ionic line.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 2. Limits of detection (LOD) and quantification (LOQ) of the method for wear metals determination in used lubricating oils by ICP OES.

Emission line (nm)	SA ^a		On-line SDA ^b	
	LOD	LOQ	LOD	LOQ
	(ng g ⁻¹)	(ng g ⁻¹)	(ng g ⁻¹)	(ng g ⁻¹)
Cd II (214.439)	10	50	20	70
Cr II (267.716)	7	20	10	40
Cu I (327.395)	20	50	6	20
Fe II (238.204)	30	80	20	80
Mn II (257.610)	2	8	4	10
Ni II (231.604)	30	90	30	100
Pb II (220.353)	200	600	200	600

^aNebulizer type: OneNeb[®] nebulizer.

^bNebulizer type: Multinebulizer.

Table 3. Analytes concentrations found in lubricating oil samples (diluted 1:10 with petroleum ether) using multinebulizer/SDA/ICP OES.

Emission line (nm)	Unused lubricating oil (A)	Used lubricating oil (B)
	Found value ($\mu\text{g g}^{-1}$) ^a	Found value ($\mu\text{g g}^{-1}$) ^a
Cd II (214.439)	< LOQ	< LOQ
Cr II (267.716)	< LOQ	2.54 ± 0.12
Cu I (327.395)	< LOQ	2.4 ± 0.2
Fe II (238.204)	0.452 ± 0.015	40 ± 2
Mn II (257.610)	< LOQ	0.46 ± 0.07
Ni II (231.604)	< LOQ	0.78 ± 0.03
Pb II (220.353)	< LOQ	1.0 ± 0.2

^a Uncertainty values are the estimated standard deviations of the extrapolated concentration.

Table 4. Analyte concentrations in three spiked used lubricating oil samples (*i.e.*, B, C and D) determined by ICP OES using SA and SDA calibration methods.

Sample	Method		Cd	Cr	Cu	Fe	Mn	Ni	Pb
B	SA	Initial ^a	<LOQ	2.7 ± 0.5	2.4 ± 0.4	40.9 ± 1.6	0.48 ± 0.02	0.79 ± 0.02	1.05 ± 0.04
		Found ^a	4.4 ± 0.2	6.77 ± 0.10	7.32 ± 0.12	45 ± 2	5.09 ± 0.02	5.12 ± 0.03	5.57 ± 0.02
		R ^b (%)	101 ± 5	96 ± 18	109 ± 19	99 ± 6	105 ± 5	99 ± 2	104 ± 4
	SDA	Initial ^a	<LOQ	2.54 ± 0.12	2.4 ± 0.2	40 ± 2	0.46 ± 0.07	0.78 ± 0.03	1.04 ± 0.02
		Found ^a	4.3 ± 0.3	7.0 ± 0.2	6.9 ± 0.3	44 ± 9	5.26 ± 0.17	5.1 ± 0.4	5.2 ± 0.4
		R ^b (%)	99 ± 6	99 ± 19	103 ± 18	94 ± 20	108 ± 6	99 ± 8	94 ± 8
	SA	Initial ^a	<LOQ	1.16 ± 0.05	4.4 ± 0.5	16.5 ± 0.6	0.95 ± 0.06	<LOQ	2.5 ± 0.06
		Found ^a	4.0 ± 0.2	5.05 ± 0.16	8.5 ± 0.2	20.5 ± 1.2	4.9 ± 0.2	4.2 ± 0.2	6.4 ± 0.3
		R ^b (%)	97 ± 5	96 ± 5	100 ± 13	100 ± 7	97 ± 7	101 ± 5	97 ± 5
C	SDA	Initial ^a	<LOQ	1.12 ± 0.06	4.13 ± 0.9	16.1 ± 0.3	0.96 ± 0.03	<LOQ	2.53 ± 0.11
		Found ^a	4.04 ± 0.11	5.0 ± 0.4	8.6 ± 0.8	20.6 ± 1.9	5.2 ± 0.5	4.19 ± 0.10	6.3 ± 0.5
		R ^b (%)	98 ± 3	94 ± 8	107 ± 16	97 ± 10	104 ± 11	102 ± 2	92 ± 8
	SA	Initial ^a	<LOQ	0.83 ± 0.04	4.2 ± 0.3	24.5 ± 1.6	0.42 ± 0.04	<LOQ	2.03 ± 0.04
		Found ^a	4.5 ± 0.2	5.7 ± 0.4	8.3 ± 0.2	28.8 ± 1.0	5.09 ± 0.02	4.55 ± 0.03	6.30 ± 0.02
		R ^b (%)	98 ± 5	106 ± 9	94 ± 7	99 ± 8	105 ± 5	99.6 ± 1.0	96 ± 2
	SDA	Initial ^a	<LOQ	0.85 ± 0.03	4.2 ± 0.6	24.4 ± 0.4	0.43 ± 0.02	<LOQ	2.01 ± 0.05
		Found ^a	4.3 ± 0.2	5.5 ± 0.3	8.2 ± 0.5	30 ± 2	4.6 ± 0.2	4.9 ± 0.4	6.3 ± 0.4
		R ^b (%)	94 ± 6	102 ± 7	91 ± 9	104 ± 11	93 ± 10	108 ± 8	94 ± 6
D	SA	Initial ^a	<LOQ	0.83 ± 0.04	4.2 ± 0.3	24.5 ± 1.6	0.42 ± 0.04	<LOQ	2.03 ± 0.04
		Found ^a	4.5 ± 0.2	5.7 ± 0.4	8.3 ± 0.2	28.8 ± 1.0	5.09 ± 0.02	4.55 ± 0.03	6.30 ± 0.02
		R ^b (%)	98 ± 5	106 ± 9	94 ± 7	99 ± 8	105 ± 5	99.6 ± 1.0	96 ± 2
	SDA	Initial ^a	<LOQ	0.85 ± 0.03	4.2 ± 0.6	24.4 ± 0.4	0.43 ± 0.02	<LOQ	2.01 ± 0.05
		Found ^a	4.3 ± 0.2	5.5 ± 0.3	8.2 ± 0.5	30 ± 2	4.6 ± 0.2	4.9 ± 0.4	6.3 ± 0.4
		R ^b (%)	94 ± 6	102 ± 7	91 ± 9	104 ± 11	93 ± 10	108 ± 8	94 ± 6

^a Uncertainty values are the estimated standard deviations of the extrapolated concentration. In $\mu\text{g g}^{-1}$.
^b R: Recovery. Spike concentrations were: 4.38, 4.10 and 4.57 $\mu\text{g g}^{-1}$, for samples B, C and D, respectively and were the same for all analytes.