

JAAS

Journal of Analytical Atomic Spectrometry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: C. Sáez, D. Stoitsov, M. Á. Aguirre, V. Kmetov, C. Coscollà and A. Canals, *J. Anal. At. Spectrom.*, 2024, DOI: 10.1039/D3JA00319A.



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.

Wear metals determination in lubricating oils by reversed-phase dispersive liquid-liquid microextraction and microwave induced plasma optical emission spectrometry

View Article Online
DOI: 10.1039/D3JA00319A

Carmen Sáez,^{a,b} Dimitar Stoitsov,^c Miguel Ángel Aguirre,^{*b} Veselin Kmetov,^{†c} Clara Coscollà,^d and Antonio Canals^{*b}

^aPublic Health Laboratory of Alicante, 6 Plaza de España, Alicante, 03010, Spain.

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

^cDepartment of Analytical Chemistry and Computer Chemistry, University of Plovdiv Paisii Hilendarski, 24 Tzar Assen Str., Plovdiv, 4000, Bulgaria.

^dFoundation for the Promotion of Health and Biomedical Research in the Valencian Region, FISABIO-Public Health, 21, Avenida Catalunya, Valencia, 46020, Spain.

[†] Deceased.

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

Abstract

A periodic study of the engine oil can allow to anticipate possible breakdowns that the vehicle could have. Due to the complexity of the matrix of this type of samples, a sample treatment prior to analysis is necessary. Analytical chemistry is constantly searching for simpler, more sensitive and environmentally friendly methods. The reversed phase dispersive liquid-liquid microextraction fulfills all the characteristics for the analysis in this type of sample by microwave induced plasma optical emission spectrometry (MIP OES). In this work, the extractant solvent used for the microextraction procedure is a diluted acid solution (i.e., 3 M HCl), which is a less-hazardous solvent, in comparison with other solvent used in microextraction procedures. Besides, it is perfectly compatible with MIP OES. The main experimental factors affecting the extraction of Cr, Cu, Mn, Mo, and Ni (i.e., amount of sample, extractant type, acid concentration, extractant volume, extractant time, and centrifugation time and speed) are optimized using a multivariate analysis consisting in two steps: a Plackett-Burman design followed by a circumscribed central composite design. Under optimum conditions (i.e., amount of sample: 5.9 g; extractant volume: 60 μ L; extractant

1 type: HCl; acid concentration: 3 M; extraction time: 3 min; centrifugation time:
2 3 min; centrifugation speed: 2000 rpm), the proposed analytical method is
3 validated and employed to analyze different samples (i.e., used and unused
4 engine oils). Two calibration methods have been evaluated since matrix effects
5 have been observed in the used engine oil sample. These effects have been
6 eliminated using standard addition calibration obtaining RSD and recovery
7 values in the range of 4-12 % and 94-106 % respectively, for samples spiked with
8 $1 \mu\text{g g}^{-1}$ of Cr, Cu, Mn, Mo and Ni. Finally, the greenness of this method has been
9 assessed by the Eco-Scale metrics.

10 11 **1. Introduction**

12 During standard engine operation, wearing is inevitable and the mechanical
13 erosion frequently introduces wear metals into the oil circulation¹. These wear
14 products are composed of the same material as the metal surfaces from which
15 they originated. Therefore, a periodic study of the engine oil could allow to
16 anticipate possible breakdowns that the vehicle could have, replacing worn parts
17 before their breakage or irreversible damage. This type of study is part of the
18 maintenance plan of maritime transport, aviation, oil refineries, mining or
19 chemical plants.² For instance, for some elements, there are limit values of
20 concentration considered abnormally high (e.g., 4-28 mg kg⁻¹ for Cr, 25-60 mg
21 kg⁻¹ for Cu, 1-3 mg kg⁻¹ for Mn, 4-20 mg kg⁻¹ for Mo and 1-5 mg kg⁻¹ for Ni)
22 although these limits are very difficult to establish due to the wear metal content
23 depends on how much the oil has been used.³ However, engine oil analysis is
24 often a difficult task due to its matrix complexity, viscosity and high organic
25 content. Hence, analytical techniques with high sensitivity are needed, as well as
26 develop efficient analytical methods. Spectrometric techniques such as flame
27 absorption atomic spectrometry (FAAS),^{1,4-6} electrothermal atomic absorption
28 spectrometry (ETAAS),⁷⁻⁹ microwave induced plasma optical emission
29 spectrometry (MIP OES),¹⁰⁻¹² inductively coupled plasma mass spectrometry
30 (ICP-MS),^{13,14} and inductively coupled plasma optical emission spectrometry
31 (ICP OES),^{2,6,15-17} have been widely used for engine oil analysis. Among all
32 analytical technique above mentioned, MIP OES stands out for having
33 advantages such as low acquisition and operating cost, multielemental
34 determination capability and suitable detection limits, and has become a useful

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

Downloaded on 12/19/2023 11:28:58 AM
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.



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

analysis tool with high stability and robustness for a variety of sample types.¹⁸

View Article Online
DOI: 10.1039/D3JA00319A

However, the lower plasma temperature compared with ICP-based technique makes the MIP OES more susceptible to matrix effects, especially with organic matrices.¹⁹ Whatever the analytical technique employed, it is evident that the quantification of low analyte concentration in engine oils is a tough task and the difficulty rises when the concentration decreases. Hence, in engine oil analysis, the direct introduction of the sample in the analytical technique is not recommended and a sample preparation must be performed.² Several sample preparation procedures are proposed in the bibliography, including: (i) engine oil dilution^{2,15,16,20} (ii) engine oil emulsification,^{1,2,4,14,20} (iii) microwave digestion,^{2,21} and (iv) (micro)extraction.⁷

The sample dilution with a miscible organic solvent is an attractive sample preparation procedure since it is quick and simple. Unfortunately, the problems associated with organic vapor loading into the plasma, such as carbon deposit generation and plasma cooling, are greatly aggravated with this procedure.²⁰ Another popular sample preparation is the microwave-assisted acid digestion. Although this procedure completely removes the organic matrix of the sample, it is time-consuming and there is a high risk of sample contamination and volatile analyte losses.²⁰ For engine oil emulsification, the most important drawbacks are the low stability of the emulsions and the samples must be diluted for the preparation of emulsions, which is detrimental to the limits of detection and quantification.²²

Regarding to microextraction procedure, it is an attractive procedure due to its simplicity, high enrichment factor and greenness. Nowadays, laboratories employ analytical methods that ensure compliance with the principles of green analytical chemistry,²³ being the reversed phase dispersive liquid-liquid microextraction (RP-DLLME), where the extractant is an aqueous solution, a consolidated green sample preparation. In this mode, a microvolume of a diluted acidic aqueous solution allows analytes to be completely separated from the organic phase with a high enrichment factor.²⁴

In this work, the RP-DLLME was proposed as green sample preparation method for the extraction of heavy metals from engine oils before MIP OES quantification. From the best of our knowledge, this is the first application combining RP-DLLME and MIP OES for the determination of metals in engine

1 oils. Finally, the greenness of this method was confirmed by the Eco-Scale
2 metrics.²⁵ View Article Online
DOI: 10.1039/D3JA00319A

3 4 **2. Experimental**

5 *2.1. Reagents and samples*

6 Calibration standards for Cr, Cu, Mn, Mo, and Ni were prepared from a
7 multielement solution (Conostan S-21, SCP Science, Baie D'Urfé, Canada) using
8 petroleum ether as a solvent (Panreac, Barcelona, Spain). In this work two
9 calibrations protocols were used, external calibration for starting experiments
10 and standard addition calibration to correct matrix effects. In both calibration
11 protocols 5 standards were prepared covering the range 0.1-3.0 mg L⁻¹.

12 External calibration:

13 The necessary amount of Conostan was taken and brought to the necessary
14 mass (i.e., 5.9 g) to reach the desired concentration by diluting with petroleum
15 ether. Subsequently, the developed method (extraction + detection) was applied
16 to all these solutions.

17 Standard addition calibration:

18 5.3 g of sample was taken and the appropriate amount of Conostan was added,
19 bringing the mixture to 5.9 g with petroleum ether. Subsequently, these
20 solutions were treated with the complete method (extraction + detection).

21 For multivariate optimization, a standard of 2 µg g⁻¹ was used with all analytes
22 and the extractant solvent was prepared from HNO₃ 65% (w w⁻¹) (Merck Pro
23 Analysis, Darmstadt, Germany) or HCl 32% (w w⁻¹) (Merck) in MilliQ water
24 (resistivity 18 MΩ cm).

25 Used engine oil was obtained from a local automobile workshop near the
26 University of Alicante. The used lubricating oils were drained from an
27 automobile engine during a routine service in a garage after use at a certain
28 mileage (20,000 km). It was stored in amber glass flasks at 4 °C. The engine oil
29 was diluted gravimetrically with a dilution factor of 10 (DF=10) with petroleum
30 ether to decrease its viscosity.

31 32 *2.2. RP-DLLME procedure*

33 For analyte extraction, a sample amount of 5.9 g was placed in a 10 mL glass
34 tube with 60 µL of extractant solvent (i.e., 3 M HCl). The mixture was shaken

1 for 3 min with a vortex-type stirrer. Afterwards, the sample was centrifuged for
2 3 minutes at a speed of 2000 rpm. Finally, the organic phase was removed, and
3 the aqueous extract (i.e., 50 μ L) was introduced into the MIP OES (**Figure 1**).
4

5 *2.3 Instrumentation*

6 The Agilent 4100 (Agilent, Melbourne, Australia) was used in this study. The
7 MIP OES instrument is equipped with a double-pass cyclonic spray chamber
8 (Glass Expansion, Victoria, Australia) and an inert OneNeb[®] nebulizer
9 (Ingeniatrics, Seville, Spain). Additional details about instrumental parameters
10 of MIP OES are shown in **Table 1**.

11 The sample introduction system of the MIP OES spectrometer was modified in
12 order to introduce low volume of aqueous extract (**Figure S1**). A pipette tip of
13 200 μ L was inserted in the sample capillary of the OneNeb[®] nebulizer. By using
14 a micropipette, a portion (50 μ L) of the aqueous extract is transferred from the
15 bottom of the sample tube to the tip. Afterwards, the spectrometer peristaltic
16 pump transports the portion of the extract to the nebulizer. After the
17 introduction of the aqueous extract, 200 μ L of MilliQ water was sequentially
18 introduced in order to rinse the sample introduction system and to prepare it
19 for the next run.

20 Statistical software (NemrodW[®] version 2007, LPRAI, Marseille, France) was
21 used for generation of the experimental design matrices and for data processing.
22 Furthermore, Statgraphics statistical computer package “Statgraphics Centurion
23 XVI” (Warrenton, VA, USA) was used to analyze the desirability function.

24 **3. Result and discussion**

25 *3.1. Optimization of RP-DLLME experimental parameters*

26 A multivariate approach was employed to optimize the main experimental
27 factors affecting metal extraction. In order to identify the most important
28 experimental factors affecting RP-DLLME procedure, a previous screening
29 experimental factors affecting RP-DLLME procedure, a previous screening
30 study (Plackett–Burman design) was carried out. After that, significant factors
31 were optimized by means of a Circumscribed Central Composite Design
32 (CCCD). In both cases, the emission signal of each analyte obtained from MIP
33 OES analysis of the resulting extractions was used as response.

1 3.1.1. *Screening study.* The investigated factors in this work were: (i) Sample weight, (ii) type of extraction phase, (iii) concentration of the extraction phase, (iv) volume of the extraction phase, (v) extraction time, (vi) centrifugation time, and (vii) centrifugation speed. Each factor was investigated at two levels, defining the upper and lower limits of the range covered by each factor (**Table S1**). The experimental plan (**Table S2**) was consisted of 12 runs which were randomly performed. Levels chosen for the different factors were based on literature data and preliminary experiments.

2 A standard containing 2 $\mu\text{g g}^{-1}$ of the analytes were used as a model sample in all the screening experiments. After the RP-DLLME procedure, the resulting analyte-enriched extract was analyzed by MIP OES, evaluating the emission signal obtained of each analyte.

3 **Figure S2** shows the Pareto charts obtained from the screening experiments. The length of the bars is proportional to the significance of the factors that affect the emission intensities of the analytes. The bars which extend beyond the dashed vertical line indicate statistically significant factors at 95% probability. Also, the direction of the bar is related to the sign of the effect produced by the corresponding factor. For example, rightward bars indicate a positive effect on the response when a factor value increases, while leftward bars indicate a negative effect during the increase of same factor value.

4 In this study, the factors affecting significantly the emission signals at the different analyte emission lines were type of extractant, sample weight and extractant volume. During the screening step, it was found that when HNO_3 is used as extractant, significantly lower emission signals were achieved for each of the investigated analyte emission lines compared to the emission signals obtained with HCl used as extracting phase. For this reason, HCl was chosen to be used as extractant in the next step of the optimization study. Meanwhile, the quantitative factors, sample weight and extractant volume, both significantly affect the responses of Cu, Mn, Mo, and Ni but in opposite directions. Increasing sample weight leads to an increase of the emission signals of the analytes, while increasing the extractant volume causes a decrease of the analyte responses. In order to make possible the RP-DLLME/MIP OES method to be used for multielement determination of Cr, Cu, Mn, Mo, and Ni in lubricating oils, all of the analytes must be determined under a set of same experimental

1 conditions. For this reason, both factors sample weight and extractant volume
2 must be optimized simultaneously and finally if it is needed compromised
3 common optimized conditions must be accepted for Cr, Cu, Mn, Mo, and Ni. As
4 a result, a circumscribed central composite design was used for the optimization
5 of sample weight and extractant volume. Finally, the other factors (i.e.,
6 concentration of the extraction phase, extraction time, centrifugation time, and
7 centrifugation speed) were fixed at the most convenient level. The concentration
8 of the extraction phase, extraction time, and the centrifugation time were fixed
9 at their high levels (i.e., HCl 3 M, 3 min, and 3 min, respectively), while the
10 centrifugation speed was fixed at its low level (i.e., 2000 rpm).

11 12 *3.1.2. Optimization study*

13 The factors that have been previously established as significant were optimized
14 in this step. The main aim of this optimization study was to find, if it is possible,
15 the optimum experimental conditions of the microextraction procedure in order
16 to achieve simultaneously the best responses for all of the analytes that were
17 evaluated. In **Table S3**, the factors and the levels investigated in the central
18 composite design are presented. This experimental design involves five levels
19 for each factor: a low level (-1), a central level (0), a high level (+1), and two star
20 points located at $\pm\alpha$ ($\alpha = 1.414$). The CCD included twelve runs which were
21 randomly performed (**Table S4**). The optimum level of each variable was
22 studied by constructing response surface plots and their corresponding contour
23 plots (**Figure S3-S7**), which were generated from the signal obtained in the
24 different experiments in **Table S4**. As can be seen, as the sample weight
25 increases the signal increases up to a maximum and then decreases. This can
26 explain as follows; the higher sample weight, the higher analyte response, but it
27 can be only valid below a critical optimum value of the sample weight for each of
28 the analytes evaluated. Sample weight higher than this optimum value may
29 worsen the dispersion of the aqueous extractant preventing the transfer of the
30 analytes from the organic phase into the aqueous extractant. On the other hand,
31 an increase in the extractant volume leads to an increase in the final volume of
32 aqueous extract in which analytes are extracted. As a consequence, an excessive
33 extractant volume could lead to a dilution effect, thus decreasing the
34 enrichment factor.

1 Because of different optimized values were obtained for the different analytes
2 (**Table S5**), a desirability function was employed. This function allows the
3 simultaneous optimization of more than one response, finding the best
4 compromise for all of them.²⁶ The overall desirability was calculated by
5 determining the geometric mean of individual desirabilities, represented in a
6 dimensionless scale (i.e., from zero to one). In this graphic, one represents the
7 wanted response and zero is the undesirable response. **Figure 2** shows the
8 desirability function and its contour plot. As a result, the desirable values for
9 simultaneous extraction of all the analytes were 5.9 g (i.e., sample weight) and
10 60 μL (i.e., extractant volume). In summary, optimal RP-DLLME conditions
11 were: 5.9 g of sample weight, 3 M HCl as the extractant phase, 60 μL of
12 extractant volume, 3 min of extraction and centrifugation time, and 2000 rpm
13 of centrifugation speed.

15 3.2. Validation of the proposed method

16 In preliminary experiments, the effect of different matrices (i.e., petroleum
17 ether and real-world matrices) for the analyte extraction was studied. In these
18 experiments, negative matrix effects were confirmed when analyzing different
19 real-world samples (results not given). As a consequence, standard addition
20 calibration was employed to evaluate the analytical figures of merit and assess
21 the applicability of the proposed analytical method under optimized extraction
22 conditions.

23 **Table 2** presents the analytical figures of merit of the proposed method using
24 standard addition calibration. Firstly, ten blanks containing the solvent
25 (petroleum ether) and unused lubricating oil (i.e., the first point of the standard
26 addition calibration) were measured after the RP-DLLME procedure and the
27 limits of detection (LOD) and quantitation (LOQ) were estimated. The obtained
28 LOD and LOQ values were estimated in the range of ng g^{-1} levels. The lowest
29 LOD and LOQ values were calculated for Cu and the highest were obtained for
30 Mo. Also, the highest sensitivity was observed for Cu in comparison with the
31 other analytes (i.e., Cr, Mn, Mo, and Ni). Moreover, the repeatability of the
32 method was tested by measuring two standard solutions containing different
33 analyte concentrations (1 and 2 $\mu\text{g g}^{-1}$, respectively). Average RSD under 10%
34 was obtained for the developed vortex-assisted RP-DLLME/MIP OES method.

1 The optimized proposed method was applied for the determination of Cr, Cu,
2 Mn, Mo, and Ni in two types of lubricating oils (i.e., unused and used oils) using
3 external calibration (i.e., without matrix effect correction) and using standard
4 addition calibration. For method validation, the following criteria for RSD and
5 recovery values were accepted: RSD<16% (Horwitz criterion),²⁷ acceptable
6 recovery percentages (80-110 %).²⁸ As it can be seen from the results in **Table**
7 **3**, the trueness of the proposed method, expressed as recovery value, is higher
8 for the determination of all analytes in unused lubricating oil than in the case of
9 used lubricating oil using external calibration. The difference between the
10 obtained recovery values for these analytes, determined respectively in unused
11 and used lubricating oil, is a proof for an existing difference between the matrix
12 composition of both types of lubricating oils. In this case, the lower recovery
13 values obtained for the analytes in used lubricating oil (**Table 3**), can be
14 explained by the fact that the dispersion of the extractant phase could be
15 different in both solvents and it was confirmed by visual inspection. In addition,
16 it must be noted that the concentrations of the analytes found in the original
17 unused lubricating oil were below the LOQ, excepting Mo. The higher
18 concentrations of heavy metals found in the original used lubricating oil can be
19 explained by taking into account the wear of metal parts of machines during
20 their operational life when such elements like Cu, Ni, Mo, Mn and Cr can be
21 accumulated into lubricating oil. It is obvious from **Table 4** that, in the case of
22 standard addition calibration, higher recovery values were obtained for Cr, Cu,
23 Mo, and Ni in comparison with the external calibration (**Table 3**). The higher
24 recovery values were a sign of the correction of matrix effect of the proposed
25 method for Cr, Cu, Mo, and Ni in unused and used lubricating oils. Only the
26 recovery value of Mn was not affected by the matrix effect of the unused
27 lubrication oil matrix if a comparison is made with the external calibration
28 method. In comparison with external calibration, it appears that standard
29 addition calibration can be chosen as more appropriate calibration strategy for
30 the determination of wear metals in lubricating oils.

3.4 Application of the Eco-Scale

31
32 In order to assess the greenness of the new RP-DLLME/MIP OES method, the
33 Eco-Scale metrics²⁵ was used to calculate the penalty points of the whole
34



analytical process. The results of which appear in **Table S6**. The result obtained in the Eco-Scale metrics was >75 , representing an excellent green analysis.

3.5 Comparison with other analytical methods

A summary of different analytical methods employed for the analysis of wear metals in lubricating oils can be seen in **Table 5**. The most commonly used sample treatment is emulsification with a surfactant agent such as Triton. In case of He et al.¹⁴ and Leite et al.,²⁹ the LOD values obtained were higher in comparison with the proposed analytical method, even with the use of more sensitive and more expensive analytical instrumentation (i.e., ICP-MS and ETAAS, respectively). In the emulsion procedure proposed by Azcarate et al.,¹⁰ the detection technique was the same as the proposed analytical method (i.e., MIP OES), providing higher LOD values. Alternatively, Carballo et al.⁸ suggested another type of emulsion in which a surfactant is not needed, but a cosolvent is used, creating a three-component solution. After a vortex agitation, it is directly introduced in ETAAS and the LOD obtained are in the range of $\mu\text{g g}^{-1}$, which are higher than those obtained in the proposed analytical method (i.e., ng g^{-1}). Tekie et al.² proposed different analytical method using ICP OES as a detection technique, obtaining the lowest LOD values using a microwave digestion mineralization, which is a time-consuming procedure. Summarizing, the application of the proposed analytical method can enhance the sensitivity of the MIP OES technique obtaining LOD values slightly lower in comparison to those obtained with ICP-MS. Furthermore, the proposed method avoids the use of time-consuming procedures such as mineralization by microwave digestion or emulsification and it solves all problems related with organic matrix in MIP OES since wear metals were extracted from complex matrix (i.e., lubricating oil) to a more compatible aqueous solution.

4. Conclusions

For the first time ever, vortex-assisted RP-DLLME/MIP OES method was proposed for the determination of the heavy metals (Cr, Cu, Mn, Mo, and Ni) in used and unused lubricating oils. The extraction method conditions were optimized by a two steps experimental design and its analytical figures of merit

1 were obtained and presented. With the optimized proposed method,
2 instrumental limits of detection and quantitation can be achieved in the range of
3 ng g⁻¹ levels for Cr, Cu, Mn, Mo, and Ni. In comparison with the concentrations
4 found for Cr, Cu, Mn, Mo, and Ni in µg g⁻¹ levels in used lubricating oils, the
5 concentrations of these elements found in unused lubricating oil are below the
6 LOQ. The higher metal content in used lubricating oils is a result from the wear
7 of metal parts of machines during their operational life, when accumulation of
8 these elements into lubricating oils can occur. Also, due to matrix effects, better
9 recovery values were obtained for Cr, Cu, Mn, Mo and Ni in lubricating oils with
10 the standard addition calibration method. Hence, standard addition calibration
11 method can be chosen as more appropriate calibration strategy for the analysis
12 of heavy metals in lubricating oils than external calibration.
13 Finally, given the importance of developing environmentally friendly analytical
14 methods, it is noteworthy that this novel and promising method is classified as
15 excellent on the Eco-scale metrics. Besides, the use of relatively cheap
16 instrumentation as MIP OES makes the proposed analytical method affordable
17 for any laboratory.

18 **Acknowledgements**

19 The authors would like to thank the Spanish Ministry of Science and Innovation
20 (PID2021-126155OB-I00), the Regional Government of Valencia (Spain)
21 (CIPROM/2021/062), and University of Alicante (UAIND21-03C) for the
22 financial support. 15% of this study is financed by the European Union-
23 NextGenerationEU, through the National Recovery and Resilience Plan of the
24 Republic of Bulgaria, project number BG-RRP-2.004-0001-C01. This article is
25 based upon work from the Sample Preparation Study Group and Network,
26 supported by the Division of Analytical Chemistry of the European Chemical
27 Society. Finally, the authors would also like to thank Agilent Technologies Inc.
28 for the loan of the MIP OES spectrometer and Ingeniatics for the OneNeb®
29 Series 2 provided. This work is part of the PhD. Degree of C. S.
30

31 **Conflicts of interest**

32 There are no conflicts of interest to declare.
33



References

View Article Online
DOI: 10.1039/D3JA00319A

- (1) Aucélio, R. Q.; de Souza, R. M.; de Campos, R. C.; Miekeley, N.; da Silveira, C. L. P. The Determination of Trace Metals in Lubricating Oils by Atomic Spectrometry. *Spectrochimica Acta - Part B Atomic Spectroscopy* **2007**, *62*, 952–961. <https://doi.org/10.1016/j.sab.2007.05.003>.
- (2) Tekie, H. A.; McCrindle, R. I.; Marais, P. J. J. G.; Ambushe, A. A. Evaluation of Six Sample Preparation Methods for Determination of Trace Metals in Lubricating Oils Using Inductively Coupled Plasma-Optical Emission Spectrometry. *South African Journal of Chemistry* **2015**, *68*, 76–84. <https://doi.org/10.17159/0379-4350/2015/v68a12>.
- (3) *Limit values for lubricants*. <https://en.oelcheck.com/wiki/limit-values-for-lubricants/> (accessed 2023-10-27).
- (4) Goncalves, I. M.; Murillo, M.; González, A. M. Determination of Metals in Used Lubricating Oils by AAS Using Emulsified Samples. *Talanta* **1998**, *47*, 1033–1042. [https://doi.org/10.1016/S0039-9140\(98\)00186-6](https://doi.org/10.1016/S0039-9140(98)00186-6).
- (5) Silveira, E. L. C.; Coelho, R. C.; Neto, J. M. M.; De Moura, C. V. R.; De Moura, E. M. Determinação de Metais Em Óleos Lubrificantes, Provenientes de Motores de Ônibus Urbano, Utilizando a FAAS. *Quimica Nova* **2010**, *33*, 1863–1867. <https://doi.org/10.1590/S0100-40422010000900008>.
- (6) Vähöja, P.; Välimäki, I.; Heino, K.; Perämäki, P.; Kuokkanen, T. Determination of Wear Metals in Lubrication Oils: A Comparison Study of ICP-OES and FAAS. *Analytical Sciences* **2005**, *21*, 1365–1369. <https://doi.org/10.2116/analsci.21.1365>.
- (7) Aguirre, M. Á.; Canals, A.; López-García, I.; Hernández-Córdoba, M. Determination of Cadmium in Used Engine Oil, Gasoline and Diesel by Electrothermal Atomic Absorption Spectrometry Using Magnetic Ionic Liquid-Based Dispersive Liquid-Liquid Microextraction. *Talanta* **2020**, *220*, 121395. <https://doi.org/10.1016/j.talanta.2020.121395>.
- (8) Carballo, S.; Terán, J.; Soto, R. M.; Carlosena, A.; Andrade, J. M.; Prada, D. Green Approaches to Determine Metals in Lubricating Oils by Electrothermal Atomic Absorption Spectrometry (ETAAS). *Microchemical Journal* **2013**, *108*, 74–80. <https://doi.org/10.1016/j.microc.2013.01.002>.

- 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
- (9) Andrade, J. M.; Carballo-Paradelo, S.; Terán-Baamonde, J.; Carlosena, A.; Soto-Ferreiro, R. M.; Prada-Rodríguez, D. Multivariate Calibration to Implement Green ETAAS Methods when Analysing Cu in Lubricating Oils. *Analytical Methods* **2013**, *5*, 4039–4046. <https://doi.org/10.1039/c3ay40410b>.
- (10) Azcarate, S. M.; Langhoff, L. P.; Camiña, J. M.; Savio, M. A Green Single-Tube Sample Preparation Method for Wear Metal Determination in Lubricating Oil by Microwave Induced Plasma with Optical Emission Spectrometry. *Talanta* **2019**, *195*, 573–579. <https://doi.org/10.1016/j.talanta.2018.11.045>.
- (11) Nelson, J.; Gilleland, G.; Poirier, L.; Leong, D.; Hajdu, P.; Lopez-Linares, F. Elemental Analysis of Crude Oils Using Microwave Plasma Atomic Emission Spectroscopy. *Energy and Fuels* **2015**, *29*, 5587–5594. <https://doi.org/10.1021/acs.energyfuels.5b01026>.
- (12) Poirier, L.; Nelson, J.; Gilleland, G.; Wall, S.; Berhane, L.; Lopez-Linares, F. Comparison of Preparation Methods for the Determination of Metals in Petroleum Fractions (1000°F+) by Microwave Plasma Atomic Emission Spectroscopy. *Energy and Fuels* **2017**, *31*, 7809–7815. <https://doi.org/10.1021/acs.energyfuels.7b00654>.
- (13) Yousef Al-Dalahmeh; Al-Swaidan, H. M.; Al-Ghamdi, A. H. Combination of Ultrasonication and Induced Emulsion Breaking for Efficient Extraction of Wear Metals from Lubricating Oils with Inductively Coupled Plasma–Mass Spectrometry Determination. *Journal of Analytical Chemistry* **2019**, *74*, 71–80. <https://doi.org/10.1134/S1061934819010039>.
- (14) He, Y. M.; Zhao, F. F.; Zhou, Y.; Ahmad, F.; Ling, Z. X. Extraction Induced by Emulsion Breaking as a Tool for Simultaneous Multi-Element Determination in Used Lubricating Oils by ICP-MS. *Analytical Methods* **2015**, *7*, 4493–4501. <https://doi.org/10.1039/c4ay03024a>.
- (15) Nham, T. T.; Bombelka, R. M. Determination of Metals in Lubricating Oil by ICP-OES. *Agilent Technologies* **1991**.
- (16) Kuokkanen, T.; Perämäki, P.; Välimäki, I.; Rönkkömäki, H. Determination of Heavy Metals in Waste Lubricating Oils by Inductively Coupled Plasma-Optical Emission Spectrometry. *International Journal of Environmental*



- 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
- Analytical Chemistry* **2001**, *81*, **89–100**, New Article Online
DOI: 10.1039/D3JA00319A
<https://doi.org/10.1080/03067310108044347>.
- (17) García, M.; Aguirre, M. Á.; Canals, A. A New Multinebulizer for Spectrochemical Analysis: Wear Metal Determination in Used Lubricating Oils by on-Line Standard Dilution Analysis (SDA) Using Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES). *Journal of Analytical Atomic Spectrometry* **2020**, *35*, 265–272. <https://doi.org/10.1039/c9ja00255c>.
- (18) Balaram, V. Microwave Plasma Atomic Emission Spectrometry (MP-AES) and Its Applications – A Critical Review. *Microchemical Journal* **2020**, *159*, 105483. <https://doi.org/10.1016/j.microc.2020.105483>.
- (19) Jung, M. Y.; Kang, J. H.; Choi, Y. S.; Lee, D. Y.; Lee, J. Y.; Park, J. S. Analytical Features of Microwave Plasma-Atomic Emission Spectrometry (MP-AES) for the Quantitation of Manganese (Mn) in Wild Grape (*Vitis Coignetiae*) Red Wines: Comparison with Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). *Food Chemistry* **2019**, *274*, 20–25. <https://doi.org/10.1016/j.foodchem.2018.08.114>.
- (20) Vähöja, P.; Välimäki, I.; Roppola, K.; Kuokkanen, T.; Lahdelma, S. Wear Metal Analysis of Oils. *Critical Reviews in Analytical Chemistry* **2008**, *38*, 67–83. <https://doi.org/10.1080/10408340701804434>.
- (21) Filho, V. R. A.; Gomes, J. A. Different Lubricating Oil Treatments for the Determination of Cu, Cr, Fe, Ni, Sb, Pb, and Zn by HR-CS FAAS. *Analytical Letters* **2008**, *41*, 1555–1570. <https://doi.org/10.1080/00032710802122115>.
- (22) Vicentino, P. O.; Cassella, R. J. Novel Extraction Induced by Microemulsion Breaking: A Model Study for Hg Extraction from Brazilian Gasoline. *Talanta* **2017**, *162*, 249–255. <https://doi.org/10.1016/j.talanta.2016.10.032>.
- (23) Gałuszka, A.; Migaszewski, Z.; Namieśnik, J. The 12 Principles of Green Analytical Chemistry and the SIGNIFICANCE Mnemonic of Green Analytical Practices. *TrAC - Trends in Analytical Chemistry* **2013**, *50*, 78–84. <https://doi.org/10.1016/j.trac.2013.04.010>.
- (24) Vidal, E.; Lorenzetti, A. S.; Álvarez, M. B.; Domini, C.; Aguirre, M. Á.; Vidal, L.; Canals, A. Reversed-Phase Dispersive Liquid–Liquid

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

Microextraction for Elemental Analysis of Gasoline by Inductively Coupled
Plasma Optical Emission Spectrometry. *Journal of Analytical Atomic
Spectrometry* **2021**, *36*, 2338–2345.
<https://doi.org/10.1039/D1JA00259G>.

View Article Online
DOI: 10.1039/D3JA00319A

(25) Gałuszka, A.; Migaszewski, Z. M.; Konieczka, P.; Namieśnik, J. Analytical
Eco-Scale for Assessing the Greenness of Analytical Procedures. *TrAC -
Trends in Analytical Chemistry* **2012**, *37*, 61–72.
<https://doi.org/10.1016/j.trac.2012.03.013>.

(26) Derringer, G.; Suich, R. Simultaneous Optimization of Several Response
Variables. *Journal of Quality Technology* **1980**, *12*, 214–219.
<https://doi.org/10.1080/00224065.1980.11980968>.

(27) Thompson, M. (ed). The Amazing Horwitz Function. AMC Technical Brief.
Royal Society of Chemistry **2004**, 17.

(28) Gustavo González, A.; Ángeles Herrador, M. A Practical Guide to Analytical
Method Validation, Including Measurement Uncertainty and Accuracy
Profiles. *TrAC - Trends in Analytical Chemistry* **2007**, *26*, 227–238.
<https://doi.org/10.1016/j.trac.2007.01.009>.

(29) Leite, C. C. Determination of Fe, Cr and Cu in Used Lubricating Oils by ET
AAS Using a Microemulsion Process for Sample Preparation. *Analytical
Methods* **2015**, *7*, 3363. <https://doi.org/10.1039/c5ay00128e>.

Table 1. Instrumental parameters of the MIP OES.

Instrumental parameter	Value
Nebulization gas flow rate (L min ⁻¹)	0.70
Liquid flow rate (μL min ⁻¹)	100
Integration time (s)	1
Replicates	3
Plasma observation position	0
Background correction	Automatic
Emission lines (nm)	Cr (425.433) Cu (324.754) Mn (403.076) Mo (379.825) Ni (352.454)

Table 2. Estimated analytical figures of merit of RP-DLLME/MIP OES method.

Analyte	Linear range ($\mu\text{g g}^{-1}$)	Sensitivity (cps g μg^{-1}) ^a	r^b	LOD (ng g ⁻¹) ^c	LOQ (ng g ⁻¹) ^c	RSD (%) ^d	RSD (%) ^e
Cr	0-3	40800 \pm 900	0.9990	21	71	11	5
Cu	0-3	195000 \pm 4000	0.9991	3	9	10	6
Mn	0-3	39200 \pm 900	0.9990	34	114	7	5
Mo	0-3	62600 \pm 1400	0.9991	45	149	10	9
Ni	0-3	31500 \pm 400	0.9994	34	112	6	3

^aSlope \pm standard error. The calibration standards are five.^bCorrelation coefficient. The calibration standards are five.^c10 blanks (Petroleum ether) measured with MIP OES after RP-DLLME procedure.^dRSD obtained with 5 standard solutions containing 1 $\mu\text{g g}^{-1}$ of the analytes.^eRSD obtained with 5 standard solutions containing 2 $\mu\text{g g}^{-1}$ of the analytes.

Table 3. Determination of Cr, Cu, Mn, Mo, and Ni in unused and used lubricating oils, in the original and after dilution, using external calibration.

Analyte	Spiked value ($\mu\text{g g}^{-1}$)	Unused lubricating oil			Used lubricating oil		
		Found concentration* ($\mu\text{g g}^{-1}$)	Recovery (%)	Original concentration ($\mu\text{g g}^{-1}$)	Found concentration* ($\mu\text{g g}^{-1}$)	Recovery (%)	Original concentration ($\mu\text{g g}^{-1}$)
Cr		<LOQ		<LOQ	0.121±0.002		1.21±0.02
	1.05	0.98±0.02	93±2	9.8±0.2	1.030±0.014	86.3±1.1	10.30±0.14
Cu		<LOQ	-	<LOQ	1.25±0.11	-	12.5±1.1
	1.05	0.883±0.010	84.1±1.1	8.83±0.10	1.92±0.05	64±12	19.2±0.5
Mn		<LOQ	-	<LOQ	0.550±0.013	-	5.50±0.13
	1.05	0.99±0.03	94±3	9.9±0.3	1.412±0.014	81.8±1.0	14.12±0.14
Mo		0.160±0.008	-	1.60±0.08	0.99±0.04	-	9.9±0.4
	1.05	1.073±0.011	86.9±0.2	10.73±0.11	1.58±0.03	57±6	15.8±0.3
Ni		<LOQ	-	<LOQ	0.121±0.008	-	1.21±0.08
	1.05	0.90±0.03	86±3	9.0±0.3	0.97±0.03	81±3	9.7±0.3

*DF=10

Table 4. Determination of Cr, Cu, Mn, Mo, and Ni in unused and used lubricating oils, in the original and after dilution, using standard addition calibration.

Analyte	Spiked value ($\mu\text{g g}^{-1}$)	Unused lubricating oil			Used Lubricating oil		
		Found concentration* ($\mu\text{g g}^{-1}$)	Recovery (%)	Original concentration ($\mu\text{g g}^{-1}$)	Found concentration* ($\mu\text{g g}^{-1}$)	Recovery (%)	Original concentration ($\mu\text{g g}^{-1}$)
Cr	1.05	<LOQ		<LOQ	0.15±0.03	-	1.5±0.3
		1.02±0.11	97±10	10.2±1.1	1.21±0.08	101±9	12.1±0.8
Cu	1.05	<LOQ	-	<LOQ	1.46±0.12	-	14.6±1.2
		1.02±0.12	96±12	10.2±1.2	2.57±0.09	106±9	25.7±0.9
Mn	1.05	<LOQ	-	<LOQ	0.81±0.08	-	8.1±0.8
		0.99±0.10	94±10	9.9±1.0	1.92±0.04	106±9	19.2±0.4
Mo	1.05	0.16±0.07	-	1.6±0.7	1.62±0.12	-	16.2±1.2
		1.23±0.10	102±9	12.3±1.0	2.66±0.10	99±10	26.6±1.0
Ni	1.05	<LOQ	-	<LOQ	0.28±0.04	-	2.8±0.4
		1.11±0.12	106±12	11.1±1.2	1.371±0.004	103±4	13.71±0.04

*DF=10

Table 5. Comparison of the different analytical methods used for the analysis of wear metals in lubricating oils.

Analytes	Sample Preparation	Detection Technique	LOD	Reference
Cr, Cu, Mn, Mo and Ni	RP-DLLME vortex assisted with HCl 3 M	MIP OES	3-45 ng g ⁻¹	This work
Ag, Al, Ba, Ca, Cd, Cr, Cu, K, Mg, Mn, Mo, Ni, Pb, Si, Sn, Ti, V and Zn	Emulsion with xylene and Triton X-114	MIP OES	0.46-2.09 µg g ⁻¹	10
Mg, Cu, Ni, Cu and Pb	Extraction induced by emulsion breaking with Triton X-114	ICP-MS	9-126 ng mL ⁻¹	14
Ag, Ba, Cu, Mn and Ni	Microwave digestion with nitric acid	ICP OES	1.07-18 ng g ⁻¹	2
Fe, Cr and Cu	Emulsion with kerosene, Triton X-100, HNO ₃ and n-propanol	ETAAS	0.04-1.85 µg g ⁻¹	29
V, Ni, Cu, Cr, Pb, Mo and Ag	Emulsion with MIBK, HNO ₃ , HCl and n-propanol	ETAAS	0.14-0.70 µg g ⁻¹	8

Open Access Article. Published on 15 December 2023. Downloaded on 12/19/2023 11:11:11 AM.
 This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.



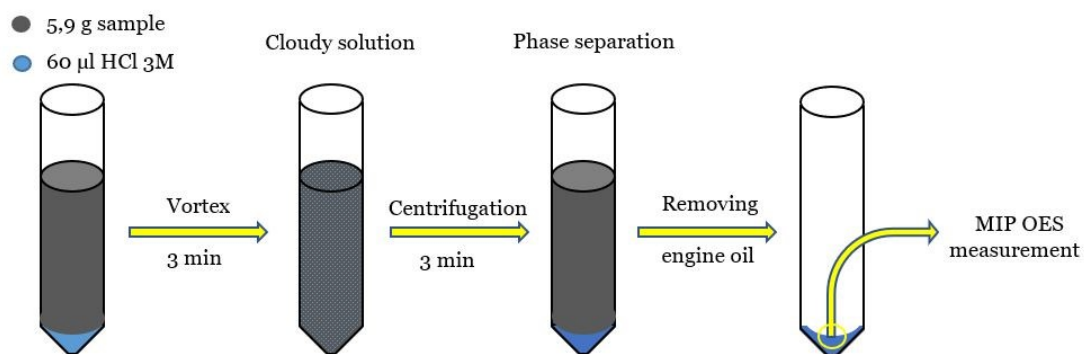


Figure 1. Scheme of the analytical procedure for Cu, Ni, Mn, Mo and Cr quantification.

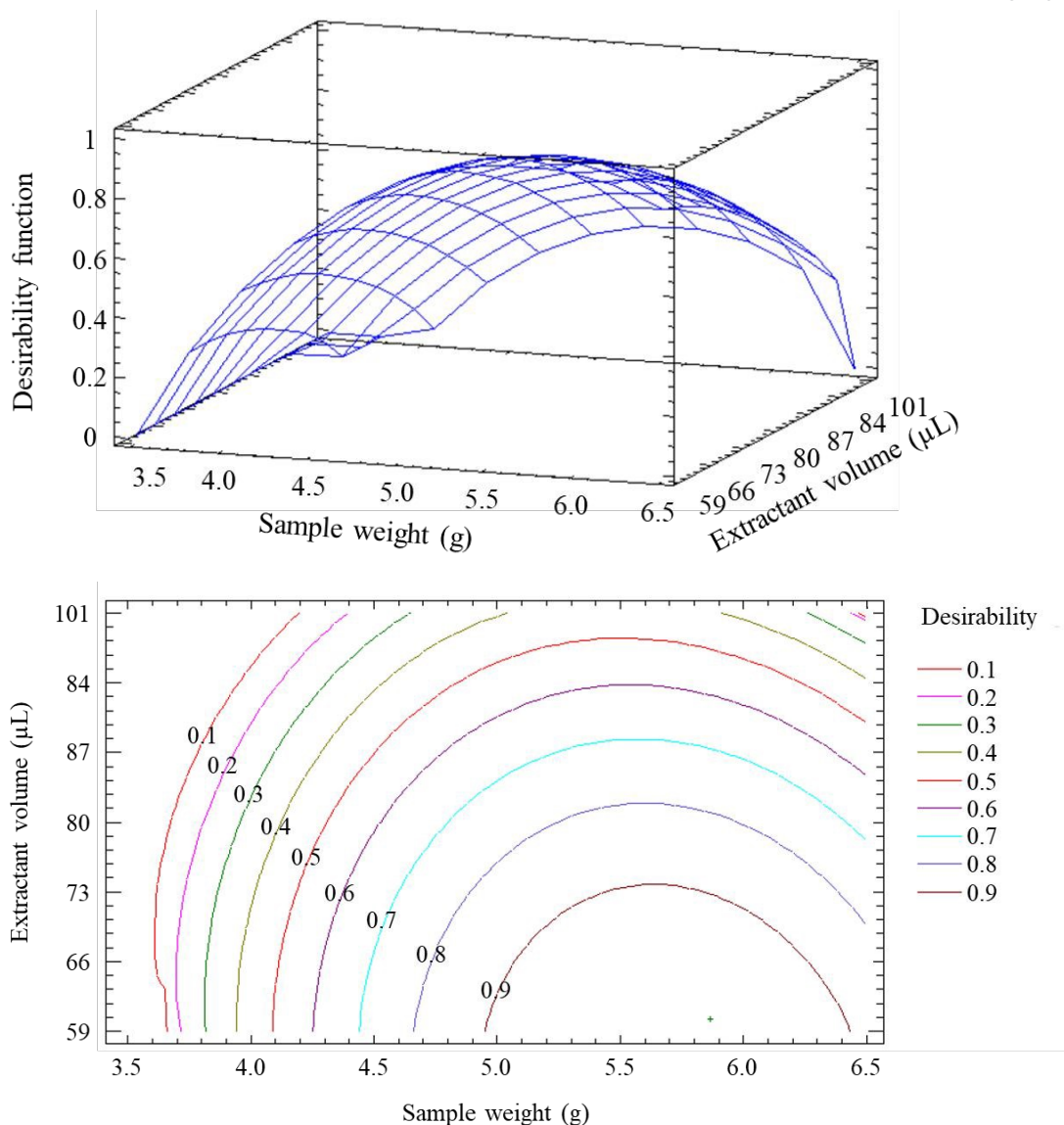


Figure 2. The desirability function and its contour plot.