

Analysis of wear metals in lubricating oils using the new MultiNeb[®] in ICP-OES

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1. Introduction

The systematic monitoring of wear metals in oils employed to lubricate engines is an essential and cost-effective preventive maintenance. Routine tracking is indispensable to minimize the premature bearing failure and to avoid costly repairs and unplanned downtime. Analysts are mainly concerned with wear metals like Ni or Cr which indicates corrosion in bearings or pistons, respectively. Another example less specific is the concentration of Fe which indicates corrosion in various parts of the engine. 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, flame atomic absorption spectrometry (FAAS) has been used extensively to monitor trace wear metals in used oils. However, the high sample throughput has forced many laboratories to use alternative multi-element analysis techniques. ICP-OES is an excellent alternative and it is as well the preferred technique in the ASTM method D 5185-18 for the analysis of lubricating oil [1].

Nevertheless, the main limitation of this analysis lies in its matrix complexity. The organic nature of the sample itself generates matrix effects and its high viscosity hampers the proper sample introduction. Moreover, the high organic solvent load and the formation of carbon deposits on different places of the plasma torch (e.g., injector and/or tulip) impose serious difficulties and practical problems. Moreover, it is widely known that direct introduction of organic sample (*i.e.*, after sample dilution) into the plasma is fraught with several drawbacks, requiring the optimization of instrumental and operating parameters and/or special calibration techniques [2].

The new MultiNeb[®] [3] is an innovative nebulizer for plasma-based techniques that eliminates the carbon deposits on the tulip torch and at the tip of the injector caused by the high organic solvent load in ICP-OES by the simultaneous introduction of organic samples and aqueous calibration standards, avoiding the use of organic calibration standards. The MultiNeb[®] 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. Another remarkable characteristic is that the unique configuration of the MultiNeb[®] enables to carry out on-line calibration methodologies. A powerful calibration method called standard dilution analysis (SDA) has been recently proposed, which simultaneously combines the advantages of the standard addition (SA) and internal standard (IS) calibration methodologies [4]. Hence, the combination of both MultiNeb[®] and SDA method results in a synergetic association for organic samples analysis with minimal sample pretreatment.

2. Experimental

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.

Table 1. Optimum operating conditions.

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
Replicate read time (s)	1
Total liquid uptake rate (mL min ⁻¹)	2.5
Organic sample uptake rate (mL min ⁻¹)	0.5
Aqueous standard uptake rate (mL min ⁻¹)	2.0
Blank standard uptake rate (mL min ⁻¹)	2.0
Nebulizer type	MultiNeb® nebulizer
Spray chamber	Cyclonic spray chamber
<i>Emission lines measured (nm)</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)

The nebulizer used in this study was a multiple nebulizer MultiNeb® [5] (**Figure 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 [6,7].

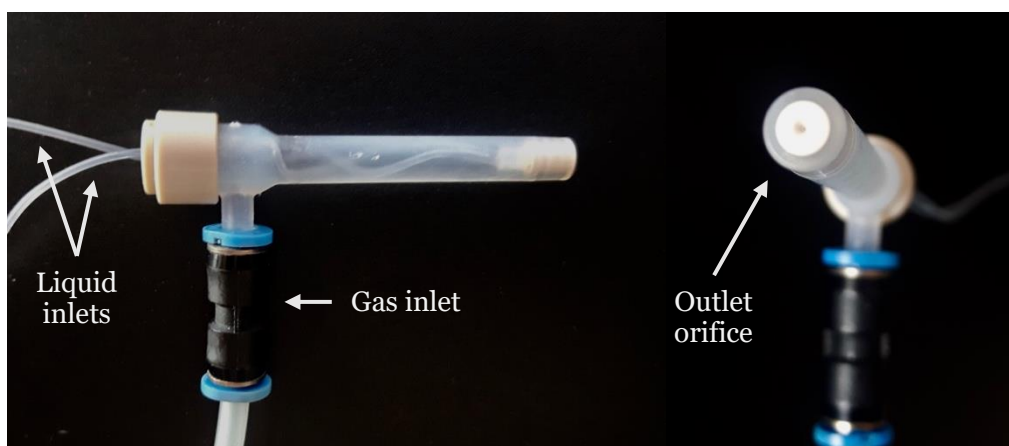


Figure 1. Side view (left) and front view (right) of the MultiNeb® multiple nebulizer prototype.

The liquid sample introduction system was composed by the mentioned MultiNeb[®] nebulizing 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 MultiNeb[®] nebulizer 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 peristaltic tubes were used depending on the liquid: (i) for organic solutions, a peristaltic tube compatible with most petroleum-based products (F-4040-A, id. 0.76 mm, Ismatec, Switzerland) was employed; and (ii) for aqueous solutions, a Tygon[®] peristaltic tube (R-3607, id. 1.65 mm, Ismatec) was used.

2.2. On-line SDA methodology

The on-line SDA methodology was performed using three channels of the peristaltic pump. A scheme of the system is shown in **Figure 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 calibration standard with the aqueous calibration blank. Finally, the channel 3 (flow rate: 2.0 mL min^{-1}) was employed to aspirate aqueous calibration standard (*i.e.*, analytes and internal standard). Additional details on the mathematical approach used for calculation of concentrations using SDA methodology can be found elsewhere [4]. The same analysis using conventional SA calibration was employed for comparison.

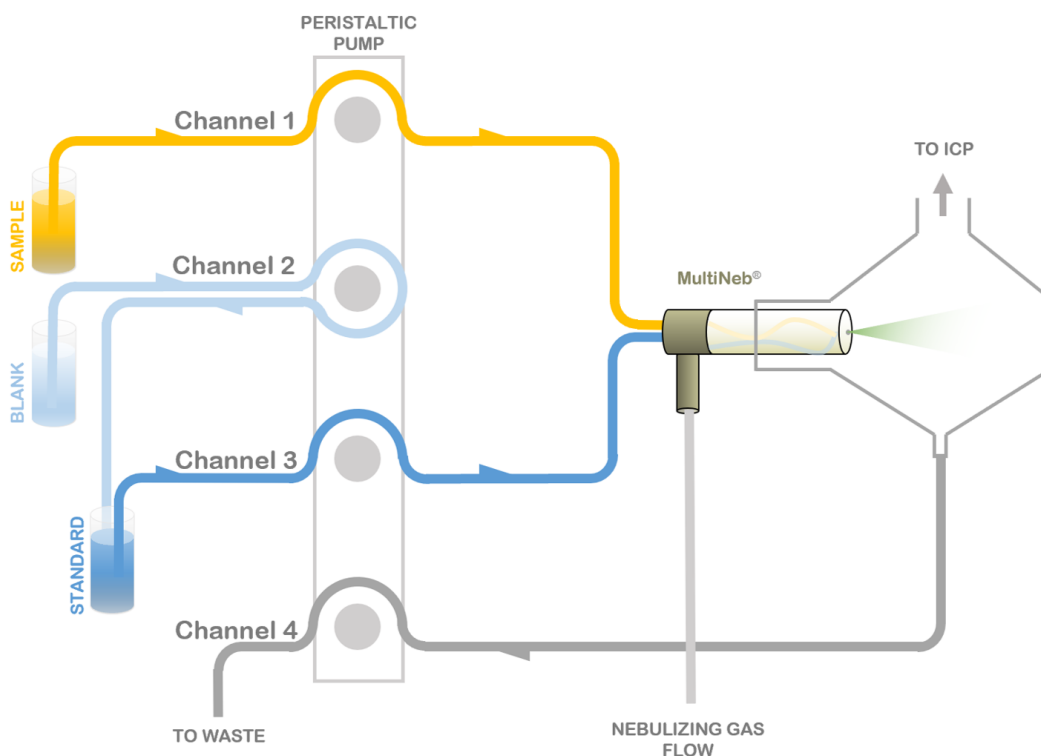


Figure 2. Scheme of the proposed on-line SDA using the MultiNeb[®] multiple nebulizer.

2.3. Sample and reagents

2.3.1. Organic samples. Samples of lubricating oil were provided from different local car workshops. An unused lubricating oil (*i.e.*, sample A) and used lubricating oils (*i.e.*, samples B-D) were employed as real-world samples. Used lubricating oils were drained from different car engines during a routine service at a garage after usage at certain mileage (*i.e.*, 20,000 km). They were labelled and stored in amber glass flasks at 4°C. All oil samples were gravimetrically diluted (1:10) with petroleum ether (QP, Panreac, Barcelona, Spain. Boiling range: 190–250 °C) in order to decrease their viscosity. An organic calibration blank containing petroleum ether was also prepared. Moreover, the results obtained with on-line SDA were compared with a conventional SA calibration. Six organic calibration standards of 0.2, 0.4, 0.6, 0.8, 1.0 and 5.0 $\mu\text{g g}^{-1}$ were prepared using Conostan standard solution (SCP Science, Baie D'Urfé, Canada). The solvent used in these calibration standards was also petroleum ether and the blank calibration standard was also prepared using this solvent.

2.3.2. Aqueous calibration standard. An aqueous calibration standard of 4 $\mu\text{g g}^{-1}$ was prepared by appropriate dilution of a multielemental Merck IV stock solution from Merck (Darmstadt, Germany) containing 1000 $\mu\text{g g}^{-1}$ 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 M Ω cm resistivity) and the aqueous calibration blank was also prepared using this solvent.

2.3.3. Auxiliary organic calibration standard. When on-line SDA is applied (**Figure 2**), organic sample and aqueous calibration standards are pumped with different liquid flow rates (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 calculated using the MultiNeb[®] system described 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 [7].

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. **Figure 3** shows an on-line SDA signal profile for one of the model analytes investigated in this study. Three steps were required to apply the on-line SDA methodology using the MultiNeb[®] nebulizer. First, the organic (channel 1) and the aqueous (channel 3) calibration 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 calibration blank (channel 2) was added to the aqueous calibration standard with the same flow rate, which resulted in the continuous dilution of the aqueous calibration standard, that was continuously aspirated by the nebulizer (step 3). Finally, when a stable minimum is obtained, calibration blanks were introduced again (step 1) to rinse the system and ready it for the next run (**Figure**

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 [4]. **Figure 4** shows the calibration curve corresponding to the signal graph shown in **Figure 3**. As it can be seen in **Figure 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.

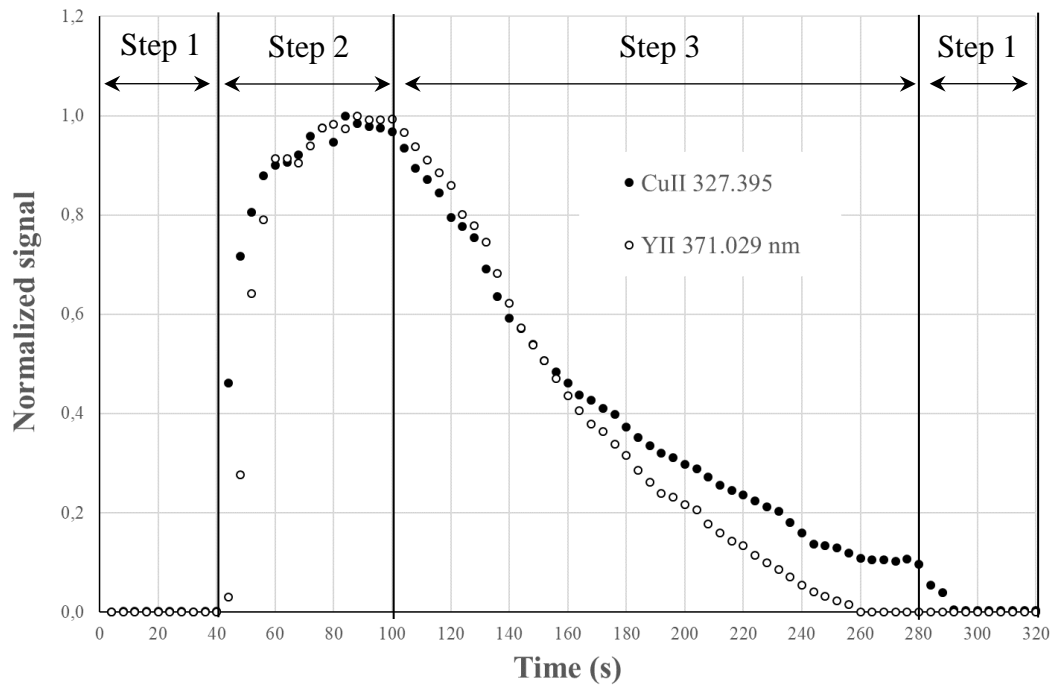


Figure 3. On-line SDA signal profile for determination of Cu in samples with organic matrix.

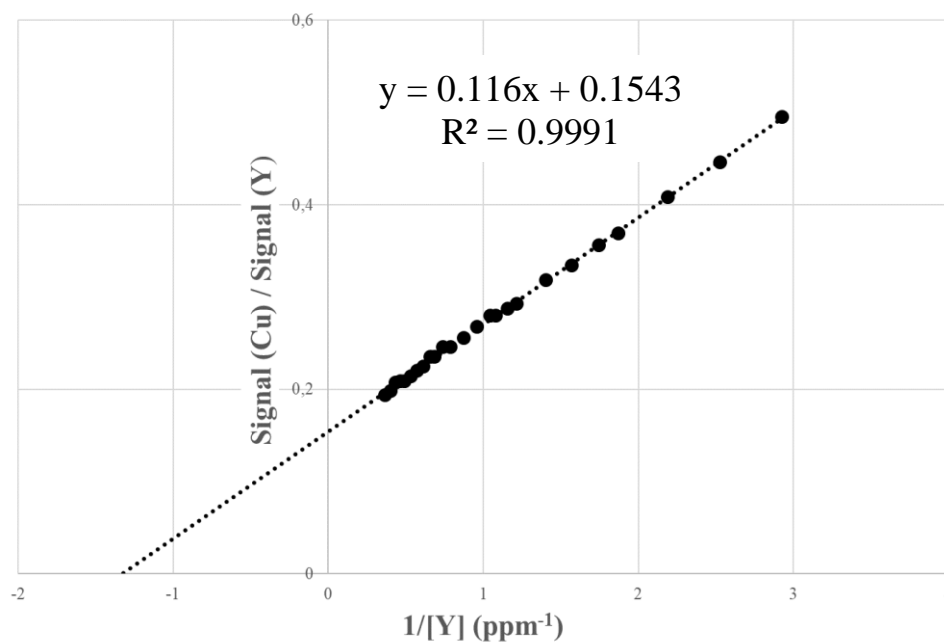


Figure 4. On-line SDA calibration curve for determination of Fe in samples with organic matrix.

3.2. Limits of quantification (LOQ)

Table 2 shows the limits of quantification (LOQ) for determination of wear metals obtained using both calibration methodologies (*i.e.*, on-line SDA and conventional SA). According to Eurachem guidelines [8], LOQ is calculated by most conventions to be the analyte concentration corresponding to the obtained standard deviation at low levels (*i.e.*, standard deviation of 10 replicates of the blank) multiplied by a factor, *k*. The IUPAC default value for *k* is 10 [9]. LOQ values obtained using on-line SDA calibration were similar or slightly higher than those obtained with conventional SA 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**, LOQ values obtained with both are in the same order of magnitude. This is a compromise between the negative effects of organic solvents [10] and the positive effects of aqueous solutions [11]. Even though, the MultiNeb[®] 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 LOQ. However, the synergistic combination of the MultiNeb[®] and the SDA calibration strategy provides LOQ values which are fit for purpose with remarkable advantages over conventional SA calibration method, as handling simplicity, significant reduction in the total analysis time, number of solutions to be prepared, and reagent and sample consumption.

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

Emission line (nm)	SA	On-line SDA
	LOQ (ng g ⁻¹)	LOQ (ng g ⁻¹)
Cd II (214.439)	47	73
Cr II (267.716)	23	42
Cu I (327.395)	49	21
Fe II (238.204)	84	75
Mn II (257.610)	8	14
Ni II (231.604)	90	106
Pb II (220.353)	614	642

3.4. Analysis of real-world samples

The MultiNeb[®]/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 from **Table 3**, the found concentration values in sample A (*i.e.*, unused lubricating oil) were below the LOQ, with the exception of iron, while the concentration values found in samples B-D (*i.e.*, used lubricating oil) were higher than those obtained in sample A for all the evaluated analytes, except for cadmium in samples B-D and nickel in samples C-D. This confirms the change in the elemental composition of the lubricating oil after a certain kilometers of 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 [12]. In any case, limit values are difficult to establish since these

elements have multiple sources and the wear metal content depends on the kilometers. 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 information provided from the component manufacturer, the oil supplier company and/or experienced analysts.

Table 3. Found concentrations in unused and used lubricating oil samples (90% dilution) determined by on-line SDA in ICP-OES.

Emission line (nm)	Unused lubricating oil (A)	Used lubricating oil (B)	Used lubricating oil (C)	Used lubricating oil (D)
	Found value ($\mu\text{g g}^{-1}$)	Found value ($\mu\text{g g}^{-1}$)	Found value ($\mu\text{g g}^{-1}$)	Found value ($\mu\text{g g}^{-1}$)
Cd II (214.439)	< LOQ	< LOQ	< LOQ	< LOQ
Cr II (267.716)	< LOQ	2.54 ± 0.12	1.12 ± 0.06	0.85 ± 0.03
Cu I (327.395)	< LOQ	2.4 ± 0.2	4.13 ± 0.09	4.2 ± 0.6
Fe II (238.204)	0.452 ± 0.015	39.8 ± 2	16.1 ± 0.3	24.4 ± 0.4
Mn II (257.610)	< LOQ	0.46 ± 0.07	0.96 ± 0.03	0.43 ± 0.02
Ni II (231.604)	< LOQ	0.78 ± 0.03	< LOQ	< LOQ
Pb II (220.353)	< LOQ	1.0 ± 0.02	2.53 ± 0.11	2.01 ± 0.05

4. Conclusions

In this study, it has been demonstrated that the new MultiNeb[®] multiple nebulizer is valid for on-line SDA of wear metals and additives in used lubricating oils by ICP-OES. The proposed analytical methodology (i.e., MultiNeb[®]/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 sample needs a minimal pretreatment (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, MultiNeb[®] nebulizer is robust and easy to handle (iv) lower organic solvent consumption, as only aqueous standards are used; (v) no carbon deposits on different places of the plasma torch (e.g., injector and/or tulip); and (vi) 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, and more economical analytical methodology for the analysis of used lubricating oils/organic samples/real-world samples by ICP-OES.

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