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Rapid Procedure to Determine Wear Metals in Lubricating Oils and the Analysis of Variance in the Evaluation of Sample Preparation Procedures

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Abstract. A new sample treatment is proposed based on a partial wet digestion in closed reactors assisted by microwaves for wear metal determinations by flame atomic absorption spectrometry (FAAS). It is rapid, precise and sensitive and allows the use of inorganic standards. Problems concerning solubility have been overcome with mixed solvents. The repeatability, stability, calibration curve and limit of detection were established. Six samples, with different degree of wear were analyzed for Fe, Cu, Pb and Cr by FAAS using the procedure proposed and other sample treatment procedures from the literature. Pb and Cr were not found in all samples. The one-way analysis of variance for Fe applied to each sample confirms the need of an acid attack and the importance of HCl for the digestion. The results obtained for Cu led us to use a two-way analysis of variance for all the samples considering the preparation procedures and the samples as variation sources. It showed no significant differences for the preparation procedures used. Therefore, treatments implying the use of acids are recommended when several wear metals are analyzed. On the other hand, the differences between the simple dilution and the procedures, implying the dissolution of metallic particles is an index to predict an imminent engine failure.

Key words: Wear metals; lubricating oils; flame atomic absorption spectrometry; analysis of variance.

Wear metal analysis in used lubricating oils has long been recognized to allow an effective and practical preventive engine maintenance.

There is a great variety of different procedures of sample preparation published and two reviews appear in the bibliography [1, 2]. The classical ashing is time consuming and is prone to analyte loss and contamination. Microwave digestion with acids in closed vessels avoids these problems [3] and allows the determination of the total metal content but it limits the oil amount to be treated. The procedure described in the manuals provided with the microwave ovens only allows the treatment of 0.5 g of used oil which gives detection limits too high to predict an engine failure by FAAS. The determination by GFAAS would be possible but this technique is more expensive, less accurate and required longer times [4]. The treatment of larger amounts of oil is not successful since the pressure developed is too high. One can find simple dilution procedures used in industry and others dilution procedures that imply the use of small amounts of acids. The results obtained in most important engine failure cases are very different. The presence of suspended metallic particles is the principle responsible for the dispersion of the wear metal concentration found depending on the sample treatment used. In fact, engine failures often are not predicted by simple dilution as sample treatment.

In recent years, we have developed two methods, both based on the use of acids with the aim to determine the total wear metal content in the lubricating oils. One of them [5] involves a slight acid treatment just to dissolve the metal particles followed by dilution with organic solvents. The other one [6] is based on the destruction of the organic matter by acid digestion assisted by microwaves. This procedure in spite

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of ensuring the total dissolution of the metallic particles showed several drawbacks such as: long time for sample treatment, low sensitivity and certain risk of explosion due to the high reactivity of this kind of samples. For these reasons, a double objective is pursued with this paper: to develop a rapid and safe procedure, based on a partial digestion of the organic matter and to compare some representative procedures published in the literature by means of the analysis of variance (ANOVA). The evaluation of the analytical results are made under the perspective of analytical minimalism [7] to keep analytical processes as simple as possible with the minimum resources.

Six samples of used marine lubricating oils were analyzed using different sample treatments. In all cases, flame atomic absorption spectrometry was chosen to determine Fe, Cu, Pb and Cr, since it is economical, rapid, selective and sensitive enough to predict engine failure.

Experimental

Sampling

The samples were obtained hot from running engine, to provide a homogeneous and representative sample; they were stored in poly propylene bottles.

Procedures

In all cases 2 grams of used oil were weighed into the appropriate vessel, after shaking the sample container vigorously.

Simple Dilution Procedure (A)[8]. Reagents. Nitric acid 70% (Panreac, *p.a.*), isobutyl methyl ketone (IBMK) (Panreac, *p.a.*), isopropyl alcohol (IPA) (Panreac, *p.a.*), multielemental standard aqueous solution ICP IV (Merck).

Add 1 mL of $HNO_3(c)/H_2O$ (1/1) to the oil weighed and dilute to 25 mL with the mixed solvent IBMK/IPA (4/1). The procedure for the standard set is identical applying unused oil and adding the corresponding amount of a multielemental stock solution.

Slight Acid Attack Followed by Dilution Procedure (B)[5]. Apparatus. A hot plate J.P. Selecta (1000 w).

Reagents. Nitric acid 70% (Panreac, *p.a.*), hydrochloric acid 35% (Panreac, *p.a.*), isopropyl alcohol (IPA) (Panreac, *p.a.*), Tergitol type 15-S-3 (Sigma), isobutyl methyl ketone (IBMK) (Panreac, *p.a.*), 1000 $\mu g\ g^{-1}$ multielemental standard aqueous solution ICP IV (Merck), 50 µg/g multielemental standard solution prepared by dilution with IPA/Tergitol (4/1).

Add 1 mL $HCl(c)/HNO_3(c)$ (6/1) to the oil weighed. Heat on a hot plate for 20 min. Dilute to 25 mL with IBMK/Tergitol (4/1).

The standards are prepared in the same way but with unused lubricating oil spiked with the corresponding amount of a 50 µg/g multielemental stock solution in IPA/Tergitol (4/1).

Proposed Procedure (C). Apparatus. Microwave oven CEM MDS. 2000, equipped with perfluoroalkoxy (PFA) vessels (120 mL, 220 psi).

Reagents. Nitric acid 70% (Panreac, *p.a.*), isobutyl methyl ketone (IBMK) (Panreac, *p.a.*), isopropyl alcohol (IPA) (Panreac, *p.a.*), Triton X-100 (Panreac, *p.a.*), 1000 µg/g multielemental standard aqueous solution ICP IV (Merck), 50 µg/g multielemental standard solution prepared by diluting with IPA/Triton X-100 (3/2).

This procedure is described for three PFA vessels in microwave oven. Add 2 mL of nitric acid concentrated to the oil weighed in the PFA vessel, close the vessel and place in the microwave oven. The program consists of four steps of 2 minutes each at 20% power and maximum pressures 50, 100, 150 and 200 psi. Open the reactors and allow to cool until room temperature. Transfer the product to a 25 mL flask and dilute with the mixed solvent IBMK/Triton X-100 (3/1).

The standards are prepared in the same way but with the unused oil and spiked after digestion with the corresponding amounts of a 50 µg/g multielemental stock solution in IPA/Triton X-100 (3/2). Warning: do not spike samples before digestion, since it implies risk of explosions.

Classical Ashing Procedure (D)[9]. Apparatus. A muffle oven HERON 10-PR/200 model 74, a hot plate J.P. Selecta (1000 w).

Reagents. Hydrochloric acid 35% (Panreac, *p.a.*), Potassium hydrogensulfate (Panreac, *p.a.*), multielemental standard aqueous solution ICP IV (Merck).

Weigh the used oil in a porcelain crucible. Heat until dryness. Transfer to a muffle oven at 600 °C during one hour. When cool add 1 g of $KHSO_4$ and heat until fusion. Add 5 mL of HCl (c) and heat gently during 30 min in a hot plate to dissolve the residue. Scrape the bottom, filter and dilute to 50 mL with distilled water.

The standard set for calibration consists of multielemental aqueous solutions.

Determination Technique

The determinations of Fe, Cu, Pb and Cr were carried out using a Pye Unicam 929 AA spectrometer with air-acetylene flame.

Statistical Analysis

Analysis of variance was performed with the computer software StatGraphics version 4.0.

Results and Discussion

Development of a Rapid Procedure in Closed Reactors and Metal Determination by FAAS

Influence of Sample Amount, Amount of HNO_3, Dilution Reagents and Microwave Oven Program. The aim was to develop a procedure of sample preparation that allows the treatment of enough amount of oil (>1 g) to determine wear metals by FAAS. It is based on a rapid partial digestion (just to ensure the dissolution of the metallic particles) in closed reactors assisted by microwaves.

Three samples were prepared as follows: 7 mL of HNO_3 (c) were added to 1.5 g of lubricating oil in closed reactors. A program of quick digestion for three reactors consisting of 20% power, 50 psi maximum pressure and 7 min was set based on previous work [6]. The products of a partial digestion were diluted with Tergitol or Triton X-100 to 25 ml but no absorbance signals were obtained by FAAS probably due to the high viscosity of the surfactants. The same experiment was repeated but with spiked oils and we obtained low signals with relative standard deviations (RSD) smaller than 6%. The next step consisted of using the surfactant mixed with IBMK in several ratios to dilute the oil digested with the aim of lowering the viscosity and increasing the signal. The results obtained were better for the IBMK/Triton X-100 than when IBMK/Tergitol was used. In both cases a clear and homogeneous solution was not obtained. The next step was to reduce the volume of HNO_3 (c) to 2 mL to avoid this problem.

Three samples were prepared weighing 1.5 g of used oil, adding 2 mL of HNO_3 (c) and running the same program described above for three reactors. The digestion product was diluted to 25 mL with IBMK/Triton X-100 (3/1). Fe and Cu were determined by FAAS obtaining high absorbance signals and good repeatability.

Later studies aimed to increase the amount of oil treated to 2 g keeping the final dilution volume to 25 mL so that the sensitivity was higher. Our experience in previous works [6, 10] and the bibliography [11] led us to modify the program so that the reaction was gentle and progressive to avoid membrane rupture due to overpressure. The program selected was: five steps of one minute duration at 20% power and 50, 70, 90, 150 psi of maximum pressure respectively. The volume of HNO_3 was kept at 2 mL. After partial digestion, the samples were diluted to 25 mL with IBMK/Triton X-100 (3/1). The absorbances obtained (0.236 for Fe) were higher than in the case described above for 1.5 g of oil (0.097 for Fe) and showed repeatibility. The signal increases are not only due to the higher oil amount but also to the program modification that influences the viscosity.

Once the variables were established for the used oils, we tried to check them for the standards prepared with unused oil spiked with the multielemental aqueous solution. But, the small volumes of multielemental solution added were enough to give a heterogeneous mixture and therefore no linear response. To solve this problem, an intermediate standard of 50 µg/g (from the 1000 µg/g multielemental aqueous solution with a solvent with lower polarity than water) was prepared to overcome the solubility problems [5]. The IPA/Triton X-100 mixed solvent was tested at several ratios obtaining better results with the 3:2 relationship. However, even in this case we found solubility problems and lack of linearity. Therefore, the microwave oven program was modified to get a homogeneous solution between the digested oil and the dilution reagents. The new program tested consisted of increasing the time to 8 min, 4 steps of 2 min each at 20% power and maximum pressure 50, 100, 150 and 200 psi, respectively. The standard solutions prepared as described were homogeneous. A blank and an used oil were also prepared by the same way, obtaining finally for standards and samples high signals and low RSD (between 0.0 and 4.7%).

The instrumental conditions were previously optimized and they are shown in Table 1.

Figures of Merit. The repeatability of the results for standards and samples (RSD%) was evaluated with 11 standards of unused oil spiked with 2 µg/g and 11 replicates of an used lubricating oil.

In order to establish the calibration graph a set of standards from 0.05 µg/g to 25 µg/g in wear metals was prepared and the absorbances registered. The equations obtained were:

$$y = 0.0419x + 0.0542 \ (R^2 = 0.9993) \text{ for Fe;}$$
$$y = 0.0637x + 0.0163 \ (R^2 = 0.9979) \text{ for Cu;}$$

$$y = 0.0280x + 0.007 \ (R^2 = 0.9938) \text{ for Pb and}$$
$$y = 0.0260x + 0.001 \ (R^2 = 0.9997) \text{ for Cr.}$$

The sensitivity was taken as the calibration curve slope. The detection limit was taken as the metal concentration in the unused oil, giving an absorbance equal to that of the blank mean plus three times its standard deviation. Fe was found, as expected, contaminating the unused oils, coming from the steel containers. Therefore, the Fe detection limit is higher than in the case in which the unused oil were free from this metal. All these results are shown in Table 2.

The stability was also examined by measuring periodically the absorbances of a 5 µg/g standard and a

Table 1. Instrumental conditions

	Fe	Cu	Pb	Cr
Wavelengh (nm)	248.3	324.8	217.0	357.9
Acetylene flow rate (L/min)	1.1	1.1	0.9	1.3
Burner height	8	8	8	8
Impact bead	On	On	On	On
Bandpass (nm)	0.2	0.5	0.5	0.5
Background correction	On	On	On	On

Table 2. Figures of merit

	Fe	Cu	Pb	Cr
Standards (RSD%)	4.1	2.1	1.9	3.7
Samples (RSD%)	4.5	3.2	4.3	2.4
Linear working range (μg/g)	0.5–10	0.1–20	0.2–15	0.2–15
Sensitivity (μg/g)	0.042	0.064	0.028	0.026
Limit of detection (μg/g)	0.5	0.1	0.2	0.3

sample. The standard was stable for two days and the sample for one day.

Analytical Results

Three of the more commonly used procedures, together with the method proposed in this work, were selected with the aim of comparing the results obtained.

The procedure of simple dilution with organic solvents is the most simple and rapid. It requires usually organometallic compounds. One of these methods (procedure A) [8] was modified with the aim of using inorganic compounds to prepare the standards. It consisted of using IBMK mixed with IPA instead of IBMK and using a small amount of HNO_3/H_2O (1/1) to match the samples with the standards that require the addition of metals in acid aqueous solution. The IBMK/IPA solvent was used in the ratio (4/1). The second procedure (B) selected consisted of a slight acid attack [5] with HCl/HNO_3 (6/1) on a hot plate and diluting with IBMK/Tergitol (4/1). The third procedure was the one proposed in this work (procedure C). The classical ashing procedure [9] was also selected for comparison since it is normally used as reference. As it is known, it requires long time and is prone to contamination and loss (procedure D).

The first group of lubricating oils was obtained from the "CEPSA Spanish Oil Company". The time elapsed from the sampling from the marine engine to the analysis in the laboratory was the responsible for the lack of the repeatability obtained. As it is known, the presence of suspended metallic particles leads to problems with sampling, because of the expected precipitation of these particles at the bottom of the container during storage [12].

A second group of samples was obtained through Nautical High School of this University. Six samples were taken from ships that usually tie up in the harbour of Algeciras (Cadiz). The corresponding unused oil was also obtained to prepare the standards when required. They were analyzed in a short time after sampling to avoid the above mentioned problems.

The six samples were analyzed by triplicate, with a set of standards prepared in the same way but with the same unused oil, except in the case of classical ashing in which aqueous standards are suitable. When the classical ashing procedure was used spattering of the sample (due to water contamination of the oil from the refrigeration system) gave loss of analytes. Therefore, these marine lubricating oils can not be analyzed following this procedure and only three procedures were used for comparison.

Cr and Pb concentrations were low and only in a few cases could be detected with precision. As it is known, the sensitivity by FAAS of these two metals is low and frequently they are not relevant in the diagnosis of marine engines.

Fe and Cu were found in all samples. Therefore, the comparison of the results will be carried out only for Fe and Cu by the three procedures above mentioned. They are shown in Table 3.

Analysis of Variance

Analysis of variance is the method used to interpret the results of collaborative trials [13]. In our case, the one way analysis of variance was applied to determine

Table 3. Metal concentrations (μg/g) by triplicate in used lubricating oils

Metal	Procedure	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6
Fe	A	4.63	13.88	24.00	1.88	3.00	5.50
		4.38	13.50	23.50	1.75	2.63	4.75
		5.00	13.38	22.63	1.63	2.25	5.00
Fe	B	7.13	37.13	73.38	4.50	8.13	21.00
		8.50	37.50	70.00	4.63	8.38	21.13
		9.50	37.75	68.88	4.88	8.13	20.75
Fe	C	3.38	23.25	70.63	6.13	8.38	20.25
		4.63	25.13	74.50	6.13	7.38	18.00
		5.25	24.00	72.13	7.00	7.75	18.25
Cu	A	1.75	49.00	30.88	15.00	1.88	5.38
		1.63	49.50	30.63	14.25	1.63	5.63
		1.88	50.63	30.50	13.75	1.63	5.38
Cu	B	1.13	43.50	35.75	6.00	1.38	5.50
		1.13	45.25	34.63	5.88	1.50	5.63
		0.88	47.63	33.88	6.00	1.38	5.63
Cu	C	0.88	41.75	36.75	7.00	1.88	6.25
		1.13	41.50	35.13	6.75	1.88	5.88
		1.13	41.50	36.88	6.88	2.25	6.50

Procedure A: Simple dilution. Procedure B: Slight acid attack followed by dilution. Procedure C: Partial digestion assisted by microwaves.

Table 4. ANOVA results for Fe and Cu

		Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6
Fe	F	18.26	1214.07	713.87	163.88	210.37	392.31
	p-value	0.0028	0.0000	0.0000	0.0000	0.0000	0.0000
Cu	F	26.15	29.65	40.11	456.04	10.74	11.65
	p-value	0.0011	0.0008	0.0003	0.0000	0.0104	0.0086

statistical significant differences among the three procedures with a confidence level of 95% ($p = 0.05$).

In Table 4 the results for Fe and Cu are shown. As it can be observed, the p-values are always lower than 0.05; therefore, there are significant differences among the three procedures studied. The multiple range test was applied to establish these differences (Table 5). The following conclusions can be drawn: in all cases, the simple dilution procedure (A) provides lower concentrations than the other ones, in which an acid attack is performed. It also detects the differences between the procedure B (slight acid attack in a hot plate with HCl and HNO_3) and the procedure C (partial digestion with HNO_3 assisted by microwaves). In all cases, the results with procedure B are higher than those with procedure C, except in the oil with lower Fe contents (oil 4). It may be due to the absence of metallic particles. This illustrates the importance of the HCl to dissolve the metallic particles.

The results for Cu are very different. The oil samples show different behaviour when they are analyzed by three procedures. Therefore, the two-way ANOVA must be used since we have two variation sources (factors): sample preparation procedure and the six oils analyzed. This procedure performs a multifactorial analysis of variance and proportionate test and figures to determine the factors that have a statistically significant effect on the Fe and Cu concentrations.

The results of two way ANOVA for Fe show that there are differences between procedures ($p = 0.000$). The multiple range test establishes these differences. It indicates that the procedure A (simple dilution) gives lower concentrations than the procedures B and C (both implying acid attack). These results agree with the ones obtained when the one way ANOVA is applied separately to each one of the six oils. The confidence interval graphics for the mean help to visualize these differences and they can be observed in Fig. 1.

Table 5. Multiple range test for Fe and Cu

	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6
Fe	B > A B > C	B > A C > A B > C	B > A C > A	B > A C > A C > B	B > A C > A	B > A C > A B > C
Cu	A > B A > C	A > B A > C B > C	B > A C > A	A > B A > C C > B	C > B	C > A C > B

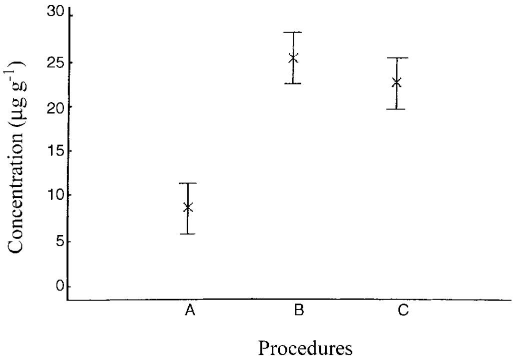

Fig. 1. Confidence interval graphic for Fe showing the differences obtained with the three procedures

The next step consisted of applying the two-way ANOVA to the analytical results obtained for Cu. In this case, there are no significant differences among the procedures ($p = 0.08$). It shows that the metal particles do not contain Cu. Therefore, to determine only Cu, the simple dilution procedure is recommended under the perspective of analytical minimalism [7] since it is more rapid and implies less reagent.

However, taking into account that usually Cu is not analyzed as only element and that Fe is indicative of general wear, the procedure B (slight acid attack with HCl and HNO_3 prior to dilution) is proposed to diagnose the engine state. In some cases, Cu has been found in the metallic particles [5, 14]. On the other hand, for Fe the differences of the results obtained by simple dilution (A) with those obtained with dissolved metal particles (B) are of interest. In the first case, only the dissolved Fe plus particles $< 1\ \mu m$ are analyzed (normal wear) [14, 15] and in the second case the iron total content is determined. As it is known in FAAS, the big metallic particles ($> 1\ \mu m$) do not reach the flame and they are not analyzed.

These differences allow a physical speciation, since it shows the type of wear that is occurring. If the differences are high it indicates that an abrasive wear (abnormal wear) is taking place and therefore, predict imminent engine failure even in samples with low wear metal concentrations [16].

Conclusions

The procedure proposed based on a partial digestion is rapid, sensitive, free from contamination and loss, the metallic particles are dissolved and the use of inorganic metal compounds as standards is possible.

The comparison of results by analysis of variance confirms the need of acids to dissolve the metallic particles, the role of HCl in cases of severe wear and the Fe as principal component of the solid particles. Therefore, it is of interest to study an acid attack prior to dilution with HCl/HNO_3 in closed reactors assisted by microwaves. A physical speciation is proposed by comparing the results obtained by the simple dilution procedures with the ones implying a prior acid attack. A significant difference would indicate the presence of big metallic particles and therefore an imminent engine failure even in samples with low wear metal concentrations.

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