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
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 polypropylene 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 HNO₃(c)/H₂O (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 μg 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)/HNO₃(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 KHSO₄ 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 HNO₃, 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 HNO₃ (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