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# Determination of Wear Metals in Marine Lubricating Oils by Microwave Digestion and Atomic Absorption Spectrometry

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**Abstract.** The difficulties associated with the development of a microwave-assisted acid digestion of lubricating oils in determination of wear metals are presented. The interest of this sample treatment lies in its basis for determining the total metal contents with enough sensitivity by flame atomic absorption spectrometry (FAAS). It allows earlier diagnosis of the engine state than is obtained by the widely applied simple dilution procedure. Another advantage is the avoidance of contamination and loss of the metals to be determined. The procedure employs nitric acid and hydrogen peroxide in a four-stage programme. Fe, Cu, Cr and Pb are determined by FAAS as representative of engine wear. The limits of detection are 0.1 µg/g for Fe and Cr and 0.05 µg/g for Cu and Pb. A comparison with other procedures is presented for spiked samples. Different types of used lubricating oils supplied by an oil company were analysed to prove the suitability of the procedure proposed.

**Key words:** wear-metal determination; lubricating oil; microwave acid digestion; flame atomic absorption spectrometry.

The determination of wear metals in used lubricating oils is of great interest in preventive maintenance of engines. The characteristics and behaviour of used marine engine oils are in many cases different from those of other lubricating oils [1, 2]. The characteristics of the sample preparation procedures commonly used for these oils are as follows. Dilution with organic solvents and acidification followed by dilution with organic solvents [3–8] leads to problems concerning repeatability, owing to the appearance of solid species (resolved in some cases with surfactants), and often the total metal content is not analysed. The traditional dry ashing and acid dissolution ASTM–IPC standard method is time-consuming and carries risk of loss and contamination. Microwave digestion with acid mixtures in closed teflon vessels avoids these problems [9] and ensures that the total metal content can be analysed, but it may give lower sensitivity in comparison to other procedures [10].

The wear metal determination requires a complicated microwave treatment, owing to the matrix and the metal concentrations in these oils. In the present work, the treatment of a larger amount of oil than that proposed by the commercial suppliers for detection of wear metals [10] was achieved in spite of the problems presented by the rapid development of a great deal of gases. The oil was digested with nitric acid and hydrogen peroxide. The metals determined were Fe, Cu, Cr and Pb as representative of marine engine wear [1]. Our aim was to destroy the organic matter and achieve total dissolution of the sample, to allow work in an aqueous medium and use of inorganic compounds as standards. This sample preparation procedure is also adequate for voltammetric metal determinations and for determining semimetals [11, 12] such as Sn and Sb, which can also be found as wear elements and require use of hydride generation methods [13].

The sample treatment procedure proposed is an interesting alternative to the classical ashing procedure and can also be used as a comparison method when dilution with organic solvents is used, to ensure

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**Table 1**. Microwave program for used oils

| Stage | Reagent added | Time (minutes) | Power (%) | Pressure (psi) |
|---|---|---|---|---|
| 1 | 10 ml $HNO_3$ (c) | 10 | 50 | 50 |
| | | 10 | 60 | 40 |
| | | 10 | 60 | 80 |
| 2 | 5 ml $HNO_3$ (c) | 10 | 70 | 125 |
| | | 10 | 70 | 200 |
| 3 | 5 ml $HNO_3$ (c) | 15 | 80 | 150 |
| | | 15 | 90 | 180 |
| | | 10 | 90 | 150 |
| | | 10 | 90 | 170 |
| 4 | 5 ml $H_2O$ $_2$ | 10 | 90 | 180 |

that the total metal content is analysed. The interest lines in the fact that the predictive capacity of the method for engine failure is higher.

## Experimental

### *Instrumentation*

A microwave oven (CEM MDS.2000) equipped with teflon vessels (PFA, 120 ml, 220 psi) and a pressure regulator. A Philips PU9200X flame atomic absorption spectrometer (Philips Analytical, Eindhoven, The Netherlands). A cryogenic bath (Haake E 1) and an ultrasonic bath (Selecta).

### *Regents*

Nitric acid, 70% (Panreac, *pro analysi*).
Hydrogen peroxide, 30% (Panreac, *pro analysi*).
1, 4-Dioxan (Merck, *pro analysi*).
Standard aqueous Cu (II) solution (1 mg/l). Prepared from $Cu(NO_3)_2 \cdot 3H_2O$ (Merck, GR).
Standard aqueous Pb(II) solution (1 mg/l). Prepared from $Pb(NO_3)$ (Merck, GR).
Standard aqueous Fe(III) solution (1 mg/l). Prepared from reduced iron (Merck, GR).
Standard aqueous Cr(III) solution (1 mg/l). Prepared from $Cr(NO_3)_3 \cdot H_2O$ (Merck, GR).

### *Sampling*

The samples were obtained from a high power cross-gear engine while the engine was running and hot, to provide a homogeneous and representative sample. They were stored in polypropylene bottles at room temperature.

### *Procedure for Wear Metal Determination in Used Oils*

This procedure is described for digesting oil samples in six perfluoroalkoxy (PFA) teflon vessels in a microwave oven. The used oil, in a polypropylene bottle, is first manually shaken and then treated in an ultrasonic bath. About 1 gram of the used oil is then weighed into each PFA digestion vessel, care being taken to avoid streaks of the oil on the vessel walls. The programme then consists of four stages.

Stage 1: 10 ml of nitric acid added per vessel, power 50% maximum pressure 50 psi, 10 min duration.
Stage 2: 5 ml of nitric acid per vessel, then four microwave steps each for 10 min, at 60% power for steps 1 and 2 and 70% for steps 3 and 4. The maximum pressures are 40, 80, 125 and 200 psi, respectively.
Stage 3: 5 ml of nitric acid per vessel, then two microwave steps each for 15 min. Step 1, power 8%, maximum pressure 150 psi. Step 2, power 90%, maximum pressure 180 psi.
Stage 4: 5 ml of hydrogen peroxide per vessel, then three microwave steps, each for 10 min at 90% power. The maximum pressures are 150, 170 and 180 psi respectively.

The samples vessels are closed throughout all the stages. Between stages, the vessels are allowed to cool down in a cryogenic bath at 5 °C, except after the last stage, when they are cooled down to room temperature. Cooling is done before the vessels are opened for addition of the reagents. After the digestion is completed and the vessels finally opened, the products are transferred into 25 ml volumetric flasks and diluted to volume with 1,4-dioxan. The whole procedure is summarized in Table 1.

The procedure for preparing the standard set for the calibration graph is identical but with 1 gram of unused oil spiked with the corresponding amounts of multielemental inorganic stock solution.

## Results and Discussion

### *Selection of the Reagents and the Microwave Oven Programme*

The digestion of lubricating oils in a microwave oven hardly appears in the literature. The only references found were a report [14] and a procedure described in the manual provided with the microwave oven the CEM corporation.

First, the method proposed by the CEM corporation [10] for used diesel oil in closed vessels was tested. It consists of weighing out 0.5 g of used diesel oil, adding 10 ml of nitric acid in the fist stage, increasing the maximum pressure gradually up to 200 psi at 30% power, and after cooling down, adding 5 of nitric acid then heating at 50% power to 150 psi maximum pressure. All this takes about 90 minutes. The sample were adequately digested, although a very thin oily film appeared on the solution surface on cooling down. With some other marine used oils, carbon residues were found in suspension after the digestion. Fe, Cr, Pb and Cu were determined by FAAS but the absorbance signals were too low for the engine state to be predicted. They can be determined by GFAAS [15], but our aim was to propose determination by FAAS, since this technique is more accurate, rapid, and less costly to purchase and maintain than is GFAAS [16, 17]. In addition, it allows a small carbon residues content [12] that would interfere with GFAAS. The treatment of larger amounts of oil than 0.5 g by the CEM method did not succeed as expected, since the pressure developed was too high.

For this reason, we decided to develop a method which could digest a higher amount of oil and thus decrease the final dilution factor. As is well known, the use of closed reactors implies risk of explosions because a great deal of gases is developed in short times. In fact, the literature indicates that if the organic content of a samples is high, the sample amount should be small. The sample amount generally used ranges from 0.1 to 0.5 g [18]. The use of oxidising acids for the digestion must also be tested very carefully because it, too, produces gases as a reaction product, and therefore, increases the inner pressure. The reactors in this microwave oven model are designed to stand pressures up to 220 psi. In addition, the method to be developed requires the destruction of the organic matrix with a minimum amount of solid residues and preferably none at all. This would allow determination of the metals by voltammetry and also determination of hydride forming elements [19]. Breaking down of fatty components requires drastic conditions [12] and the literature indicates that nitric acid, or a mixture of it with another acid could successfully destroy the oil organic matrix. On the other hand, the volume of reagents used is limited to avoid excessive dilution of the sample, and should not exceed 25 ml in order to allow dilution to 25 ml after the digestion is completed.

Taking into account all these factors, we decided to develop a method which could digest at least 1 g of marine used lubricating oils in closed reactors with a limited volume of reagents and which would develop low pressures in the first steps of each stage.

Treatment with up to 20 ml of nitric acid in one and in two stages (to avoid explosions) was tested but unsuccessfully, since total oil digestion was not achieved. With 20 ml of concentrated sulphuric acid used in two stages the product contained carbon residues and this approach was discarded. Mixtures of concentrated nitric and hydrochloric acids (15+5 ml) in two stages, concentrated nitric and perchloric acids (20+2 ml) in three stages were also tested. Neither of these mixtures was suitable, owing to either incomplete digestion of the sample or the rapid development of high pressure.

After that, we decided to test a mixture of concentrated nitric acid and hydrogen peroxide. The mixture had already been tested in a microwave oven by other authors but with other kinds of sample [12], since it is known that hydrogen peroxide has a clarifying effect after a digestion that is not complete. Twenty ml of nitric acid were added in two stages and 2 ml of hydrogen peroxide in one stage. The best results were obtained with this treatment, since the sample appeared to be completely dissolved, when the reactors were opened. Nevertheless, after cooling down, a thin oily layer appeared on the aqueous phase and, in some cases, there were small amounts of carbon particles.

All these treatments were applied with a programme of quick digestion without change in the magnetron power, the maximum pressure and the time, which were selected manually with account being take of the pressures developed.

Later studies aimed to test different ratios of nitric acid to hydrogen peroxide, the number of stages and the magnetron power and maximum pressures for programming the microwave oven. Taking into account the high reactivity of the oil with nitric acid, the heating must be gentle to avoid breakage of the safety membranes although this implies use of longer times. Therefore, we decided to investigate addition of the nitric acid in several stages, starting at low powers and increasing them at every stage. To shorten the cooling time, a cryogenic bath at 5 °C was used.

After test of different combination of stages power maximum pressures and reagent volumes, it could be concluded that the digestion of one gram of marine lubricating oil requires 4 stages, 3 stages to add 20 ml of nitric acid (10, 5 and 5 ml) and a final stage to add 5 ml of hydrogen peroxide. Three of the four stages are programmed in several steps, with increase of magnetron power and maximum pressure. With this programme, no organic residues were left on the reactor walls and hence the total digestion product could be transferred to the volumetric flask. In this way, the total metal content could be analysed. The whole procedure is described in the Experimental section and shown in Table 1.

The volume of the digestion product is between 20 and 22 ml and it must be diluted to 25 ml. If the dilution was done with distilled water, a small amount of residual organic matter from the oil appeared floating on the solution surface. This residue was found to be soluble in some organic solvents, especially in IBMK (isobutyl methyl ketone) and in strongly basic aqueous medium. It can be separated very easily, but to avoid possible losses of trace metals we looked for another solvent which, besides being miscible with water could dissolve the solid residue. Such a solvent should have an intermediate polarity. Dimethylformamide was found to dissolve the organic residue but the solution soon became turbid. With 1, 4-dioxan, the residue was totally dissolved and the sample completely transparent. Therefore, 1, 4-dioxan was the solvent selected to make the sample up to 25 ml in order to analyse for wear metals by FAAS. As is known, this solvent is suitable for AAS but can be problematic in voltammetry and in hydride generation. For use with these techniques other solvents can be tested.

### Determination of Wear Metals by FAAS

FAAS was chosen as the determination method since it is a main routine analytical technique, with many advantages. The selection of the metals to be determined was based on the composition of marine engines and should be representative enough to predict engine wear. Therefore, Fe, Cu, Pb and Cr were selected [1, 13]. The semimetals Sn and Sb can also be present in these engines, but they require hydride generation and a different methodology [19].

Several samples of used oils were prepared as described in the Experimental section and the following parameters were optimized for each element: burner height, acetylene flow rate, wavelength and impact bead position. All the metals were tested with the air–acetylene flame; for Cr the nitrous oxide–acetylene flame was tested also. The latter flame increased the sensitivity but not sufficiently to justify its use for just one element. Therefore, the four elements were all measured with the air–acetylene flame. The optimum acetylene flow rat was 1.1 min for Cu, Pb and Fe and 1.3 l/min for Cr. The burner height was always 4 mm. The impact bead was "on" in all cases. In all instances the principal wavelength was used. For Pb the secondary wavelength of 283.3 nm was also tested, as other authors have reported its use [8, 20–22] because of the high noise given by the principal wavelength. In our case, the background noise was not avoided with the 283.3 line, so the principal line was used.

**Table 2**. Repeatability of standards and samples for $n = 11$(RSD %)

| | Fe | Cu | Cr | Pb |
|---|---|---|---|---|
| Stamdards 2 µg/g (inorganic salts) | 4.3 | 3.8 | 5.2 | 5.4 |
| Standards 1.4 µg/g (organometallic compounds) | 4.5 | 4.8 | 6.1 | 4.6 |
| Samples | 1.8 | 3.6 | 3.7 | 3.0 |

The repeatability of standards and samples was evaluated with 11 standards of unused oil with 2 µg/g of the metals added as a solution of their inorganic salts. For comparison, a second study was made with the metals added as organometallic compounds (Conostan); 11 standards with 1.4 µg/g of metals added to unused oil were analysed. In both studies the metals were added to the oil before the digestion. The repeatability with used oils was also studied with 11 samples. Standards and samples were prepared as described under Experimental. The results are shown in Table 2. The comparison of the results between the two sets of standards (with inorganic and with organometallic compounds) shows that there is no difference. Therefore, the inorganic compounds are proposed because they are cheaper and more readily available. It should also be pointed out that the RSD is higher for the standards than for the samples. This may be due to the error associated with the addition of the multielement solution of the standards (this step was not required for the samples) and to the higher absorbance values for the samples; Fe is usually present in the highest concentration.

The stability of standards and samples prepared as described under Experimental was also examined. The absorbances were recorded periodically and it was found that samples and standards were stable for at least one month.

For calibration, a set of standards containing from 0.01 to 20 µg/g of each metal was prepared. Pb was measured at two wavelengths (217 and 283.3 mm) and Cr was measured with both the air–acetylene and nitrous oxide–acetylene flames. These two set of conditions had been optimized previously, but were again tested to guarantee that the metal concentration had no influence on their selection. As expected, the sensitivity for Pb was higher with the principal line (217 nm) for all concentrations tested. Chromium gave a slightly higher sensitivity with the nitrous oxide–acetylene flame, but as explained above the air–acetylene flame is recommended for the four elements. The linear working range with the optimum conditions is shown in Table 3.

The detection limit was taken as the metal concentration in the unused oil, giving an absorbance equal to that of the blank plus three times its standard deviation. The sensitivity is the relationship between concentration and absorbance. The detection limit and the sensitivity for the four metals are also shown in Table 3. The detection limit for Fe = 0.1 µg/g was obtained only when the unused oil had a low Fe content. Most unused marine lubricating oils are often contaminated with iron from the containers (usually steel) and in this case the limit of detection increases to 0.5 g/g.

In order to evaluate the proposed procedure for sample preparation (A), two samples were prepared and analysed, and the results compared with those obtained with two other established procedures: classical ashing followed by acid dissolution (B) and slight acid treatment followed by dilution with IBMK–tergitol [1] (C).

**Table 3.** Linear working range, limit of deteaction and sensitivity. All values in µg/g

| | Fe | Cu | Cr | Pb |
|---|---|---|---|---|
| Linear working range | 0.5–5 | 0.05–5 | 0.2–20 | 1–20 |
| Limit of detection | 0.1 | 0.05 | 0.1 | 0.05 |
| Sensitivity | 0.06 | 0.09 | 0.01 | 0.04 |

All elements were determined with an air–acetylene flame and at the principal wavelength.

The samples were prepared by spiking the oils with enough organometallic standard (Conostan) to get an appropriate signal by FAAS once the samples had been treated. Two different types of oils were used: Veritas Marine (sample 1) and Marino R O (sample 2), to ensure that differences between oils have no influence on the results. Two replicates of each oil were prepared and analysed. The instrumental conditions were identical for methods A and B because, in both cases, an aqueous medium was used. For method C the acetylene flow rate was lower since an organic medium was used and the wavelength used for Pb was 283.3 nm. The remaining instrumental conditions were the same. Results are shown in Table 4.

To conclude this study, three samples of different used oils were supplied by CEPSA and analysed by the proposed method with the aim of making sure whether this procedure is suitable for predicting the engine state on the basis of periodical analysis, for a wide range of oil type and engine wear. All these samples were taken from marine engineer after several thousands of working hours without change of the lubricating oil (such samples are rarely obtainable). Three different types of oil were used (Mobilgear 627, Mobilgard 412 and Superciclope). The results are shown in Table 5. With these results and some information given by CEPSA concerning wear metal analysis of the same oils but for fewer working hours, we can state the following: in the case of sample 2 the results indicate that the engine is showing a severe wear and should be submitted to inspection. Samples 1 and 3 do not show very high engine wear, but in sample 3, the Cu and Fe content is significant and therefore the oil should be analysed more frequently. The relatively high iron content in the three samples can be partly attributed to contamination of the unused oils by the containers where they are stored.

Results obtained in industry by simple dilution and AES–ICP are usually lower than those obtained by a

**Table 4.** Concentrations obtained for wear metals in µg/g by three different methods. The results are the mean of two determinations

| | Fe | | | Cu | | | Cr | | | Pb | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Samples | A | B | C | A | B | C | A | B | C | A | B | C |
| 1 | 17 | 18 | 17 | 17 | 17 | 19 | 20 | 18 | 19 | 19 | 20 | 19 |
| 2 | 22 | 19 | 19 | 17 | 17 | 21 | 20 | 20 | 20 | 19 | 18 | 19 |

*A* Proposed method.
*B* Ashing and acid dissolution method.
*C* Slight acid treatment and dilution with IMBK–Tergitol.

**Table 5**. Concentrations of wear metals in used oils in µg/g. The results are the mean of two determinations

| | Fe | Cu | Cr | Pb |
|---|---|---|---|---|
| Sample 1 | 9.6 | 3.9 | 2.4 | 1.3 |
| Sample 2 | 652 | 70 | 5.0 | 6.7 |
| Sample 3 | 75 | 79 | 4.0 | 8.5 |

particle size independent method. This is particularly relevant for the determination of Fe.

## Conclusions

The microwave procedure proposed for determination of wear metals in used lubricating oils is efficient and shows several advantages over other published procedures. This has relevant economic importance for industry. The total metal content determination ensures an early diagnosis of the engine state. The difficulties associated with the treatment of the proposed amount of samples in closed vessels successfully, overcome, and the method allows the wear metal determination by FAAS. The time required for the sample treatment could be shortened by use of reactors allowing higher pressures. The method is adequate for periodical analysis and prediction of engine wear.

The procedure for sample treatment could also be used for voltammetric metal determinations and for determination of hydride forming elements by HG-AAS. It can also be extended to edible oils and other food samples with high fatty content.

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