Determination of Wear-metals in Used Lubricating Oils From Marine Engines by Flame Atomic Absorption Spectrometry

Maria Purificacion Hernandez-Artiga and Juan Antonio Muñoz-Leyva
Analytical Chemistry Department, University of Cadiz, Puerto Real, Cadiz, Spain
Ramon Cozar-Sievert
Nautical High School, University of Cadiz, Cadiz, Spain

A method for the determination of the total content of Fe, Cu, Pb and Cr in used lubricating oils from marine engines by flame atomic absorption spectrometry is described. The influence of the sample basicity, the addition of acids, and dilution with different solvents was studied. The presence of solid species which cause serious problems concerning reproducibility was also investigated. The procedure involves the use of mineral acid to dissolve the metal particles, and a mixture of isobutyl methyl ketone and a non-ionic surfactant as solvent. The standards were prepared with aqueous inorganic salt solutions. The method is rapid and shows good sensitivity and reproducibility. A comparison is made between the results obtained from the proposed procedure and those from other atomic absorption methods.

Keywords: *Wear-metal determination; used lubricating oil; flame atomic absorption spectrometry*

The determination of wear-metals in used lubricating oils is of great interest as it allows predictions of equipment failure to be made and prompts the appropriate preventive maintenance to be undertaken. The industry requires analytical methods that can be used to carry out this determination with speed, precision and economy. Atomic spectrometry, and particularly flame atomic absorption spectrometry (FAAS), is one of the most useful techniques for such determinations.

Methods based on the ashing of the sample and acid dissolution of the residue to allow the determination of the total metal content, and the use of inorganic salts as standards, require many manipulations, are time consuming and incur the risk of contamination or loss.

Methods involving direct dilution[1–3] of the oil with an organic solvent are widely used but do not allow determination of the total metal content because the larger particles are not atomized by the flame and the results obtained are lower than those from the ashing method. In addition, these methods require the use of organometallic standards which are expensive and not readily available.

Several mixed solvent systems have been developed that permit the determination of metals by simple dilution of the sample with use of inorganic salts as standards.[4–6] Such methods are useful for metals derived from additives. However, large metallic wear-particles produced by more severe wear are not determined and several cases have been documented in which aircraft oil-wetted component failure was not predicted.[7]

Several workers have developed particle size independent methods[7–11] in which inorganic acids were added to digest the metals *in situ* followed by dilution with a mixed solvent able to dissolve oil and inorganic acids; however, the standards used were organometallic compounds or metal powder suspensions which showed poor sensitivity and precision.

The formation of stable oil–water emulsions has also been reported.[12–19] This method involves the use of aqueous inorganic standards.

All of the above methods have been developed for the analysis of aircraft, railway or automotive lubricating oils but no specific research has been applied to used marine engine lubricating oils, the characteristics and behaviour of which during sample preparation appear to be different. Simple dilution, and in particular acidification followed by dilution, causes the precipitation of solid species. This solid content leads to problems concerning reproducibility which have not been reported in the literature.

In this paper, a method is described for the determination of the total metal content in used marine engine lubricating oil. The method avoids filtration of the sample by using a homogenizing diluent which is able to accommodate the oil sample in addition to inorganic acids and aqueous inorganic standards. The metals to be determined were chosen with the aim of being able to predict the state of the engines by means of the oil analysis; therefore, the metals determined were Fe, Cu, Pb and Cr, which are representative of marine engine wear.[20,21]

Experimental

Instrumentation

The determinations were performed with use of a Philips PU9200X flame atomic absorption spectrometer (Philips Analytical, Eindhoven, The Netherlands).

Reagents

Isobutyl methyl ketone (IBMK) (Panreac, Barcelona, Spain; pro analysi).

Isopropyl alcohol (IPA) (Panreac; pro analysi).

Tergitol Type 15-S-3 (Sigma, St. Louis, MO, USA).

Hydrochloric acid, 35% (Panreac; pro analysi).

Nitric acid, 70% (Panreac; pro analysi).

Cu^{II} standard aqueous solution (1 mg dm^{-3} *of Cu*). Prepared from $Cu(NO_3)_2{\cdot}3H_2O$ (Merck, Darmstadt, Germany; GR).

Pb^{II} standard aqueous solution (1 mg dm^{-3} *of Pb*). Prepared from $Pb(NO_3)_2$ (Merck; GR).

Fe^{III} standard aqueous solution (1 mg dm^{-3} *of Fe*). Prepared from iron reduced (Merck; GR).

Cr^{III} standard aqueous solution (1 mg dm^{-3} *of Cr*). Prepared from $Cr(NO_3)_3{\cdot}H_2O$ (Merck; GR).

Sampling

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

Reference Method

Validation of the method described herein was performed by comparing the results with those obtained by FAAS after sample ashing and acid dissolution of the residue.

Procedure for Samples

Shake the sample container vigorously in order to obtain a representative sample. Weigh approximately 2 g of used oil into a 50 cm^3 Erlenmeyer flask. Add 1 cm^3 of concentrated HCl–concentrated HNO_3 (6 + 1). Heat the mixture on a hot-plate for 20 min. Allow the mixture to cool to room temperature, then dilute it to 25 cm^3 with IBMK–Tergitol (4 + 1).

Procedure for Standards

Prepare a 1000 μg g^{-1} solution of Fe, Cu, Pb and Cr from iron reduced and the corresponding nitrates with doubly distilled water. Dilute the solution to 50 μg g^{-1} with IPA–Tergitol (4 + 1). Weigh approximately 2 g of an un-used sample of the oil to be analysed and proceed as described under Procedure for Samples adding the appropriate volume of the 50 μg g^{-1} multi-element solution before diluting with IBMK–Tergitol.

A blank sample is prepared by the same method but without metals in order to establish whether the un-used oil contains trace metals.

Results and Discussion

In order to establish the behaviour of the samples, attempts were made to apply the techniques described by other workers for different types of lubricating oil. Firstly, several oil samples (5 g) were prepared by simple dilution to 50 cm^3 with IBMK and another set of samples were prepared by the same method but adding inorganic acids before diluting with IBMK. The standards were prepared in an identical manner but with the addition of metals from inorganic salts dissolved in aqueous ethanol and the same amount of un-used oil. The appearance of a fine precipitate was observed at the bottom of the container when a used oil sample was diluted with IBMK and when 1 cm^3 of mineral acid was added to used or un-used oil followed by dilution. The liquid phase was not miscible and shortly after shaking manually or ultrasonically the mixture separated into two layers. The absorbance values were not reproducible, but it could be concluded that the absorbance values were higher with the addition of acid.

The next step was to obtain a mixed solvent of IBMK and ethanol which was capable of dissolving the oil, a small amount of inorganic acid and the ethanolic solutions of the inorganic salts. Several IBMK–ethanol mixtures were tested but none was suitable. Other solvents were tried with the same aim, such as toluene, acetic acid and chlorobenzene but without success. Finally, it was found that a mixture of IBMK and IPA (4 + 1) was a suitable mixed solvent.

A set of standards of 1, 2 and 5 μg g^{-1} was prepared as follows. A mixture of 5 g of un-used oil, 1.5 cm^3 of HCl–HNO_3 (8 + 1) and the corresponding amount of the metallic salt dissolved in ethanol was diluted with IBMK–IPA (4 + 1). A precipitate appeared with the addition of acid as described above, which settled slowly to the bottom of the flask. The absorbance of this set of standards was measured by two methods: (*a*) vigorous shaking just before measuring; and (*b*) allowing the precipitate to settle to the bottom of the flask and analysing the clear supernatant liquid. The response for metals was higher with the shaken samples; however, the reproducibility was poor. It can, therefore, be concluded that the precipitate may contain metals and filtration is not advisable. The calibration graphs and reproducibility were acceptable when measuring without shaking for all the metals except Pb.

In the following experiments samples were analysed without shaking and aspirating the supernatant liquid.

Effects of Oil Basicity and Added Acid

As it had been observed that the formation of a precipitate on addition of acid did not occur with all types of marine engine lubricating oil, the total basic number (TBN) of several oils was measured following the ASTM D-2896-80 (IP 276/83) method[22] in order to relate the formation of the precipitate to the TBN value of the oil. The following experiment was carried out with use of these values: 1.5 cm^3 of concentrated HCl were added to several un-used oil samples with TBN values of about 6 and to some un-used oil samples with TBN values of about 30 followed by dilution with IBMK–IPA. The same experiment was repeated with 1.5 cm^3 of concentrated HCl–concentrated HNO_3 (6 + 1). In both instances a precipitate appeared; suddenly, when the TBN of the oil was high, and very slowly, when it was low. From these results it appears that the solid product formed could be due to the oil additives.

Several different mineral acids and mineral acid mixtures were tested. The acids tested included concentrated HCl, concentrated HNO_3, and the mixtures tested included concentrated HCl–concentrated HNO_3 [(8 + 1), (6 + 1) and (4 + 1)]. The samples were heated with the acid for 15 min on a hot-plate and diluted to 50 cm^3 with IBMK–IPA (4 + 1). The absorbance of the supernatant liquid was measured and it was found that acidifying with the 6 + 1 acid mixture gave the highest absorbance values. The heating time of the samples after addition of this mixture was investigated and the optimum heating time to attack the metallic particles was found to be 20 min.

The behaviour of used oils of different TBN values was verified by measuring the metal concentration of the samples with two sets of standards, in one instance with the addition of concentrated HCl–concentrated HNO_3 (6 + 1) and in another instance without adding acid. Two of the samples (one with a high TBN and another with a low TBN) were prepared as follows: to 4 g of used oil, 1.5 cm^3 of the 6 + 1 acid mixture were added and the mixture was heated on a hot-plate for 20 min; when the mixture had cooled to room temperature it was diluted to 50 cm^3 with IBMK–IPA (4 + 1). The other two samples were prepared by the same method but without the addition of acid. Two sets of standards were prepared following the same procedure, with the same amount of un-used oil and the addition of the corresponding aliquot of a 50 μg g^{-1} multi-element solution in IPA obtained by dilution from a 1000 μg g^{-1} stock solution in doubly distilled water. The supernatant liquid was measured leaving the precipitate at the bottom. The results are shown in Table 1.

It can, therefore, be concluded that when the oil has a high TBN value the metal concentrations obtained are higher without adding acids but when the TBN value of the oil is low the metal concentrations with addition of acid are higher for metals other than Pb.

Table 1 Concentration of the supernatant liquid. A mixture of IBMK–IPA (4 + 1) was used for the autozero

	Concentration/μg g^{-1}				
Sample	Cu	Pb	Fe	Cr	Comments
1	0.07	0.14	0.62	0.05	High TBN oil with acid attack
1	0.09	0.52	1.0	0.39	High TBN oil without acid
2	2.3	0.37	7.6	0.20	Low TBN oil with acid attack
2	2.0	0.87	6.3	0.13	Low TBN oil without acid

The results obtained with the high TBN oils could be explained by considering the two opposite effects caused by the acid attack: firstly, the solid metallic particles are dissolved, which should increase the metal concentration; however, on the other hand the precipitate formed on addition of acid carries down a portion of the metals which are, therefore, not determined and a decrease in the metal concentration found in the supernatant liquid results. Oils that have low TBN values show an increased metal concentration with added acid; therefore, in this instance the predominant effect seems to be the dissolution of the metallic particles. The behaviour of Pb is not clear, as has been found in earlier experiments and an attempt to explain it will be made later. As can be observed, the behaviour of oils with high and low TBN values is different when mineral acids are added.

Metal Content in the Precipitates

In order to prove that the precipitate formed contains metals, 4 g of a high TBN used oil sample were mixed with concentrated HCl–concentrated HNO_3 (6 + 1) and heated; when the mixture was cool, it was diluted to 50 cm^3 with IBMK–IPA (4 + 1). The precipitate that formed was separated from the liquid phase, dried in a crucible on a hot-plate and ashed in an oven at 500 °C. The insoluble residue that remained was dissolved in acid and diluted with doubly distilled water. A set of standards was prepared from a 1000 µg g^{-1} multi-element stock solution in doubly distilled water and the metal concentrations were measured by FAAS. The same experiment was undertaken with use of two standard samples containing un-used oil and with the addition of metals. The precipitate that formed from the used oil samples contained 3.2 µg of Pb, 80 µg of Fe and 4 µg of Cr. To one of the standards 125 µg of metals were added and to the other 250 µg of metals were added. The metal content of the precipitates formed from the standards was 1.5 and 2 µg of Pb, 45 and 88 µg of Fe and 72 and 73 µg of Cr, respectively. From these results it can be concluded that the precipitate from the samples and standards cannot be discarded and that analysis of the supernatant liquid alone is not satisfactory. Therefore, attempts were made to dissolve the precipitate, or to clean it from metals after separating it from the liquid with the aim of mixing the metals with the liquid phase and determining the total metal content. The precipitate was treated with H_2O_2, with KOH in ethanol and with KOH and citrate in ethanol; the mixture was heated but the results were not satisfactory.

Effect of Surfactants

The next step was to attempt to homogenize the sample using a non-ionic surfactant which should be able to maintain the precipitate in suspension; this would allow the liquid and the precipitate to be determined together. Other workers have used surfactants previously but with another purpose. Kauffman *et al.*[11] used Neodol 91–6 to stabilize the organometallic standards; they also noted that this agent widens the applicability of the method to synthetic ester oils and to hydraulic fluids. On the other hand, Salvador *et al.*[15] used Nemol K 39 to obtain an emulsion, which allowed inorganic salts to be used as standards.

Several non-ionic surfactants were tried and it was found that Tergitol Type 15-S-3 was satisfactory for maintaining the precipitate in suspension. It was intended, initially, to add a small amount of Tergitol to the mixed solvent, to dilute the sample after adding the acid mixture; however, after shaking the sample the precipitate started to settle slowly to the bottom of the vessel. It was, therefore, decided to substitute the IPA with Tergitol. Several samples were prepared, some with used oil and others with un-used oil as described under Experimental. The samples were shaken manually and it was observed that the precipitate remained in suspension. The absorbance measurements displayed good reproducibility and stability and it was, therefore, shown that Tergitol–IBMK (4 + 1) was a suitable homogenizing solvent for marine engine lubricating oil.

Instrument Parameters

Several samples were prepared by the procedure described above and the following parameters were optimized for each element: burner height, acetylene flow rate, wavelength and impact bead position. The results are shown in Table 2.

In all instances the wavelength used was the principal wavelength except for Pb, the measurement of which was made at the 283.3 nm line, as the 217 nm principal line showed a high noise, which, in many instances, exceeded the signal corresponding to the Pb content. This noise can be attributed to scattering caused by the presence of small solid particles in the flame arising from the complicated matrix of the sample, as the scattering affects measurements made at lower wavelengths.[23] When the absorbance was measured at 283.4 nm the signal-to-noise ratio was much improved. Therefore, the anomalous behaviour of Pb found previously can definitively be ascribed to the high noise level at 217 nm.

Stability and Reproducibility

The stability of several samples with a TBN value of 23 and of several standards prepared with un-used oil with a TBN value of 30 was assessed by preparing a set of multi-element standards of 1, 2 and 5 µg g^{-1} and three samples as described under Experimental. The absorbance of the standards and the concentration of samples were determined periodically, with use of IBMK–Tergitol (4 + 1) for the autozero. It was found that the samples were stable for at least 24 h and the standards for 3 d.

The reproducibility of standards and samples was evaluated with 11 standards of 2 µg g^{-1} prepared with un-used oil (TBN=30) and 11 samples with TBN values of 18 prepared as described under Experimental. The results are shown in Table 3.

Table 2 Instrument parameters

	Cu	Pb	Fe	Cr
λ/nm	324.8	283.3	248.3	357.9
Burner height/mm	8	8	8	10
Acetylene flow rate/dm^3 min^{-1}	1.0	1.0	0.9	1.2
Impact bead	On	On	On	On

Table 3 Reproducibility of standards and samples. Concentration of standards, 2 µg g^{-1}

	Cu	Pb	Fe	Cr
Standards—				
Standard deviation/µg g^{-1}	4.9×10^{-3}	1.5×10^{-3}	5.5×10^{-3}	5.2×10^{-3}
Relative error (%)	1.2	1.7	1.9	3.3
Samples—				
Standard deviation/µg g^{-1}	2.9×10^{-3}	1.0×10^{-3}	2.3×10^{-3}	1.2×10^{-3}
Relative error (%)	2.6	4.5	0.8	2.5

Table 4 Linear working range, detection limit and sensitivity. All values in µg g^{-1}

	Cu	Pb	Fe	Cr
Linear working range	0.05–5	0.2–5	0.2–10	0.5–5
Detection limit	0.01	0.01	0.05	0.5
Sensitivity	0.02	0.16	0.08	0.06

Table 5 Concentration of metals in used marine engine oils determined by the proposed method (A), flame atomic absorption spectrometry after sample ashing and acid dissolution (B), and flame atomic absorption spectrometry by simple dilution with IBMK (C). The results are the mean of two determinations

	Cu			Pb			Fe			Cr		
Sample	Method A	Method B	Method C	Method A	Method B	Method C	Method A	Method B	Method C	Method A	Method B	Method C
1	3.0	3.1	1.9	6.7	—	2.0	18	11	11	2.1	4.1	1.0*
2	3.6	3.5	2.1	7.9	11	2.4	23	28	12	5.5	5.5	2.0*
3	3.5	3.6	2.6	7.9	10	1.8	9.3	11	6.3	3.0	4.2	0.8*
4	6.7	7.3	5.7	9.5	12	3.1	24	23	15	2.6	5.7	1.0*
5	2.1	1.4	3.6	8.7	11	0.3	5.8	6.4	1.2	2.3	5.7	0.8*

* Inductively coupled plasma atomic emission spectrometry by simple dilution with kerosene.

Calibration Graph

In order to establish the calibration graph a set of standards from 0.05 to 10 $\mu g\ g^{-1}$ was prepared as described under Experimental; the linear working range is shown in Table 4. The detection limit was taken as the metal concentration in the un-used oil giving an absorbance equal to that of the blank plus three times its standard deviation. The detection limit and sensitivity are shown in Table 4.

The total content of Fe, Cu, Pb and Cr of five types of used marine engine lubricating oil was determined as described under Experimental. The results were compared with those obtained by FAAS after sample ashing and acid dissolution of the residue and with the simple dilution method with IBMK using Conostan organometallic standards. The results are shown in Table 5.

Conclusions

The data reported in Table 5 show good agreement between the results obtained with the proposed method and those from ashing of the samples; data obtained by the simple dilution method are lower. It can, therefore, be concluded that the proposed method allows the detection of the total metal content in used marine engine lubricating oil, which, as expected, is not possible with the simple dilution method.

References

1 Burrows, J. A., Heerdt, J. C., and Willis, J. B., *Anal. Chem.*, 1965, **37**, 579.

2 Kriss, R. H., and Bartels, T. T., *At. Absorpt. Newsl.*, 1972, **11**, 110.

3 Hon, P. K., Lau, O. W., and Mok, C. S., *Analyst*, 1980, **105**, 919.

4 Holding, S. T., and Rowson, J. J., *Analyst*, 1975, **100**, 465.

5 Wittmann, Z., *Analyst*, 1979, **104**, 156.

6 Wittmann, Z., *Acta Chim. Acad. Sci. Hung.*, 1982, **109**, 295.

7 Brown, J. R., Saba, C. S., Rhine, W. E., and Eisentraut, K. J., *Anal. Chem.*, 1980, **52**, 2369.

8 Kriss, R. H., and Bartels, T., *At. Absorpt. Newsl.*, 1970, **9**, 78.

9 Saba, C. S., and Eisentraut, K. J., *Anal. Chem.*, 1977, **49**, 454.

10 Saba, C. S., and Eisentraut, K. J., *Anal. Chem.*, 1979, **51**, 1927.

11 Kauffman, R. E., Saba, C. S., Rhine, W. E., and Eisentraut, K. J., *Anal. Chem.*, 1982, **54**, 975.

12 Berenguer-Navarro, V., and Hernandez-Mendez, J., *Quim. Anal.*, 1977, **31**, 81.

13 Hernandez-Mendez, J., Polo-Diez, L. M., and Bernal-Melchor, A., *Anal. Chim. Acta*, 1979, **108**, 39.

14 de la Guardia, M., Salvador, A., and Berenguer, V., *An. Quim.*, 1982, **78**, 321.

15 Salvador, A., de la Guardia, M., and Berenguer, V., *Talanta*, 1983, **30**, 986.

16 de la Guardia, M., and Salvador, S., *At. Spectrosc.*, 1984, **5**, 150.

17 Arfelli, W., *J. Test. Eval.*, 1984, **12**, 152.

18 Beferull-Blasco, J. B., de la Guardia-Cirugeda, M., and Salvador-Carreño, A., *Anal. Chim. Acta*, 1985, **174**, 353.

19 Cardarelli, E., Cifani, M., Mecozzi, M., and Sechi, G., *Talanta*, 1986, **33**, 279.

20 Taylor, C. F., *The Internal Combustion Engines in Theory and Practice*, Massachussetts Institute of Technology Press, MA, 2nd edn., 1986.

21 Frederick, S. H., and Capper, H., *Materials for Marine Machinery*, Institute of Marine Engineers, London, 1980.

22 American Society for Testing and Materials, ASTM D-2896-80 (IP 276/83), Philadelphia, PA, 1980.

23 Larson, G. F., Fassel, V. A., Winge, R. K., and Kniseley, R. N., *Appl. Spectrosc.*, 1976, **30**, 384.

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