

SHORT COMMUNICATION

APPLICATION OF A MIXED SOLVENT SYSTEM IN THE DETERMINATION OF METALS IN LUBRICATING OILS USING ATOMIC ABSORPTION SPECTROMETRY

E.O. Ojeka*

Analytical Laboratory; Department of Applied Science, C.S.T. PMB 2021, Kaduna Polytechnic, Kaduna, Nigeria

(Received April 17, 2005; revised September 13, 2005)

ABSTRACT. Analysis of lubricating oils and their additives for Ni, Zn, Mg and Ca was carried out by the proposed method using benzene-acetic acid/methyl isobutyl ketone (MIBK) mixed solvent system. Flame atomic absorption spectrometry using air-acetylene flame was employed with the incorporation of concentrated hydrochloric acid into the solvent mixture. The large dilution of samples employed due to flexible working range of this procedure eliminates the need for matched standard hence the same standards are adequate for all types of lubricating oil samples and additives. No effect on the analysis arising from varying viscosities of the oil samples was observed. Results obtained for a wide range of lubricating oils and automatic transmission fluids revealed good agreement with those obtained by established ASTM chemical procedure.

KEY WORDS: Lubricating oils, Mixed solvent system, Flame atomic absorption spectrometry, Metal determination

INTRODUCTION

Controlled amounts of added metal ions can bestow beneficial properties on lubricating oils. Metal lubricant additives provide lubricating oils with some of their important characteristics. These lubricant additives resist oxidation, reduce wear, inhibit corrosion, and improve colour viscosity-index, lubrication and combustion characteristics [1]. Metallic soaps containing magnesium and especially calcium and barium are added to lubricating oils to improve detergency, dispersibility or anti-wear properties. Zinc additives provide oxidation inhibition and anti-wear action. Nickel and calcium are extreme pressure additives [2, 3]. Most of the metals in petroleum products are in the form of organometallic compounds and hence organometallic standards are used in their determination [4]. A wide variety of materials including air, and liquids like animal, mineral, synthetic oils, emulsions, suspension and semisolids, like greases and solids like graphite, molybdenum and disulfide have been employed for lubrication purposes [2].

Wear metal determination in used lubricating oils gives an early indication of the degree of wear of the oil-wetted parts within an engine and drive train components in civilian and military vehicles. Through wear metal determination, the parts can be located and replaced before expensive engine failure occurs [3].

To our knowledge, the effect of mixing MIBK-benzene-glacial acetic acid has not been studied. The present paper examines the determination of some metals in lubricating oils and additives with acidic mixed solvent-inorganic salt standards. As far as we know, there has not been any application of this combination of extractants in literature.

*Corresponding author. E-mail: ojekaemmanuel@yahoo.com

EXPERIMENTAL

Apparatus

Element determinations were performed with a Perkin Elmer SP model 1900 flame atomic absorption spectrophotometer. Single-element hollow cathode lamps were used. All absorbance measurements were made at the 232.0 nm (Ni), 422.7 nm (Ca), 285.2 nm (Mg) and 213.86 nm (Zn) wavelengths using the respective metal hollow-cathode lamps and a band width of 0.7 nm. Sample calcinations were carried out by an electrically heated hot-plate, and muffle furnace set at between 550 °C and 700 °C, respectively.

Reagents

Deionised water was used for preparing the standard stock salt solutions. Analytical grade reagents and chemicals were employed. The metal working standard solutions were prepared by diluting 1000 µg/mL stock solutions (BDH) of each element.

Standard stock solutions of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (5.90 g); $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (8.50 g); $\text{NiSO}_4 \cdot 4\text{H}_2\text{O}$ (2.24 g) and ZnCl_2 (2.29 g) were prepared in 10 mL of 98% (v/v) MIBK to give metal ion concentrations of 10^3 , 1.016×10^3 , 5.80×10^{-2} and 1.098×10^3 mg/g, respectively. 20 mL of MIBK was added to each flask and finally diluted with glacial acetic acid to 1 L. 1.0 g of potassium acetate was added to each of the standard stock solutions to reduce ionic interferences. Methyl isobutyl ketone (MIBK) was obtained from Eastman. It was used without further purification.

Sampling

Thirty samples of lubricating oils and brake fluids in well stoppered plastic containers were purchased from same retailers (open shops) and commercial outlets in Kaduna, Nigeria. The samples were stored in refrigerator under 4 °C prior to analysis. To avoid any possible difference due to sampling, the samples for both the reference and the proposed method were drawn simultaneously. Engine oils were commercial motor-grade manufactured by Unipetrol (SAE 20W-30), Mobil (SAE 30) and Texaco (SAE 40), Nigeria. Automatic transmission-fluids (brake fluids) were obtained from the same sources.

Sample pretreatment

The oil sample was heated to 70 °C and was agitated to a homogenous suspension. The sediment was allowed to settle and then finally transferred from a 250 mL beaker to a 500 mL volumetric flask and further agitated violently. The suspended sediment was strained through a 100-mesh screen to remove large solid particles. The strained oil was further heated prior to analysis by flame AAS.

Procedure

To remove organic materials about 10 g of homogenous sample (above) was weighed into a platinum dish. The dish was heated with a Bunsen burner until the contents ignited and burnt readily. The dish and flaming contents were moved to a hot plate to complete the combustion into ash and carbon. The residue was ignited in a furnace at 550 °C and cooled. Two drops of 18 mol/L H_2SO_4 was added, followed by evaporation of the acid and the residue was again ignited to 700 °C to complete the oxidation of carbon. 0.5 g of the ash was weighed and mixed with 10 mL MIBK in a separatory funnel, and the funnel was stoppered and shaken vigorously for about

10 min. The mixture was then diluted with 1:2 (v/v) benzene-glacial acetic acid and 5 mL of concentrated hydrochloric acid was added to the mixture with shaking. The aqueous and organic phases were separated. The amount of oil in the organic phase was determined gravimetrically after igniting the samples in a furnace at 700 °C; while samples of aqueous phase were analysed using a Perkin Elmer Atomic Absorption Spectrophotometer (AAS) SP model 1900. The quantification of the amount of oil in the organic phase (though not compulsory) helps to ascertain the (rough) value of distribution coefficient of the solvent mixture.

The lubricating oils and brake fluids with widely differing composition and viscosities were analyzed and compared to a single mixed standard made up in benzene-acetic acid-MIBK, with no matching of standards to samples required. The primary aim of application of mixed solvents for this work is the technical need for solubility. The choice of this mixture as diluent ensures the dissolution of all lubricating oils and additives.

Comparison with established method

To check further the procedures discussed in this work, twenty-four of the oil samples from open shops and commercial outlets were chosen. The criterion for selection was the availability of both the samples and correlation data. "Correlation data" here is intended to mean "same samples of same batch and from same retail outlet". These samples were analysed in triplicate on a "single sample" basis using the modified ASTM standard method of chemical analysis of metals in new and used lubricating oils [5]. The residue was treated with 20 mL of 6 mol/mL HCl and evaporated to moist dryness. 25 mL of water was added and transferred to a 400 mL beaker, then diluted to 100 mL and neutralized with drops of NH₄OH and methyl red serving as indicator. 8 mL of 12 mol/L HCl and 1 g (NH₄)₂SO₄ were added. The solution was brought to boil; H₂S was passed in, until the solution cooled to room temperature. 200 mL of water was added and the solution was again saturated with H₂S solution. The filtrate was used to determine zinc, nickel, calcium and magnesium.

RESULTS AND DISCUSSION

Flame atomic absorption spectrophotometric analysis was adopted because of its availability and the fact that it offered high sensitivity comparable to other modern instrumentation namely ET-AAS, ICP-OES, ICP-MS and INAA currently available for metal analysis. By the incorporation of hydrochloric acid into the solvent system, the systematic error arising from the use of air-acetylene flame is eliminated. However, particular attention was given to fine and steady control of the gas flow in order to minimize small significant flame fluctuations, more so, with calcium determination since atomization in the flame is particularly dependant on the flame temperature. The use of high temperature introduced a potential ionization interference and was therefore avoided by the use of an excess of a more easily ionizable potassium acetate to suppress this effect. No matching of standards to sample was required. Also, atomic absorption has an advantage which does not require that standards closely match samples; necessitating a large number of different standards and knowledge of the characteristics of the samples.

Preliminary investigations show that heating the solution of the sample to 700 °C in the pretreatment procedure and the addition of the acid (HCl) to the solvent mixture was effective in obtaining full recoveries of metals from the oil as sample preparation chemically oxidized all particles to soluble salts. The presence of acid is also necessary to match the metal compounds in the sample solutions with those in the reference solution.

Direct analysis requires organometallic compounds for preparation of standards and does not permit determination of total content as only smaller particle area is analysed. On the contrary, the use of solvent mixture allows the use of inorganic salts in the preparation of standards,

taking advantage of the solubility of either inorganic salts of the element of interest or the water of crystallization of these salts. Furthermore, the destruction of organic material permits the oxidation of all particles to soluble salts, thus total metal content of the oil can be determined as in Table 1.

Table 1. Mean values of metals ($\mu\text{g/g}$) in lubricating oils and brake fluids from selected marketing organizations as obtained by the proposed method and ASTM standard method.

Element	Unipetrol				Mobil				Texaco			
	ATF by AAS ($\mu\text{g/g}$)	Unused engine oil by AAS	Used engine oil by AAS	Engine oil by ASTM method	ATF by AAS ($\mu\text{g/g}$)	Unused engine oil by AAS	Used engine oil by AAS	Engine oil by ASTM method	ATF by AAS ($\mu\text{g/g}$)	Unused engine oil by AAS	Used engine oil by AAS	Engine oil by ASTM method
Ni	55.0 ± 0.00	43.33 ± 0.006	60.00 ± 0.04	58.50 ± 0.00	55.0 ± 0.003	58.50 ± 0.02	61.00 ± 0.00	65.10 ± 0.00	60.00 ± 0.01	59.0 ± 0.01	68.0 ± 0.005	68.0 ± 0.00
Ca	0.78 ± 0.001	23.60 ± 0.001	13.0 ± 0.03	13.50 ± 0.008	1.40 ± 0.003	26.70 ± 0.001	26.0 ± 0.03	25.0 ± 0.001	7.20 ± 0.001	2.50 ± 0.003	14.0 ± 0.01	12.55 ± 0.003
Mg	1.50 ± 0.004	2.85 ± 0.02	5.50 ± 0.05	3.35 ± 0.00	1.55 ± 0.003	3.41 ± 0.008	3.10 ± 0.05	3.65 ± 0.005	4.75 ± 0.001	4.35 ± 0.08	4.80 ± 0.003	4.0 ± 0.001
Zn	0.150 ± 0.008	3.00 ± 0.001	3.55 ± 0.02	3.25 ± 0.004	1.50 ± 0.006	3.87 ± 0.003	5.00 ± 0.04	5.20 ± 0.00	0.30 ± 0.001	0.35 ± 0.01	3.5 ± 0.001	3.50 ± 0.005

ATF: automatic transmission fluid (or brake fluid). Each value is the mean \pm standard deviation of 3 trials.

Table 2. Benzene-glacial acetic acid/MIBK extractions at pH 2.

Element	Concentration of aqueous standard (mg/L)	μg extracted with 10 mL MIBK	Absorbance of aqueous standards	Absorbance of extract	Enhancement obtained
Ni	30	300	0.028	0.148	5.3
Ca	30	300	0.016	0.092	5.8
Mg	30	300	0.091	0.499	5.5
Zn	20	200	0.075	0.388	5.2

Solvent mixture selection was done on the basis of predicted distribution coefficient (capacity), separation factors and specific physical properties. Among classes of solvents, Lewis acids (alcohols and carboxylic acids) provide much better selectivity for a given capacity than do Lewis bases (ketones, esters, amines) [6]. Branching on the alcohol solvent molecule appears to be of benefit also. Selectivity was significantly affected by the amount of potassium acetate present and in the preliminary investigations, a marked improvement of selectivity for MIBK-benzene system with increasing (weight-percent) potassium acetate was noticed. It appears that the use of MIBK quantitatively transfers the oil from aqueous mixtures to the organic phase. It also has low solubility in water coupled with the use of inorganic salts standards in the aqueous phase. This behaviour may be useful in solvent recycling due to reduction in solvent loss. Furthermore, when benzene-acetic acid-MIBK mixed solvents were used, the interferences that result in differences between standards and samples were removed.

Table 1 indicates variation in the metal contents of these oils probably due to the differential requirements of the individual metal by the consumer oil companies for the improvement of lubricant characteristics. The differences in result by the proposed and reference ASTM methods adopted for this work arise probably from the fact that matrices take longer to digest in one oil sample than the other, and this may cause variation in results for the total elements determined in these samples. The chemical state of the element determined may also differ wholly or partly from one oil sample to another, or even in the same sample. This introduces variation into the

breakdown of molecular species or hinders releases from bindings with high molecular weight (polymer-based oil and brake fluids) organic molecules to the inorganic species measured. The heating stage in the pre-treatment procedure is recommended as part of the preparation of all the samples to enhance full metal recovery.

The differences in the value of magnesium by the two methods could be that magnesium improves detergency, dispersability and antiwear properties in lubricating oils and different companies depending on their production control process may use different amount of metallic soaps containing magnesium, calcium and barium. But more importantly, looking at the result in Table 1, there is a bias towards the ASTM standard method (except Texaco). Therefore, coupled with the LOD of $0.54 \mu\text{g g}^{-1}$ of the proposed method and $0.42 \mu\text{g g}^{-1}$ of the ASTM method the correct values of magnesium are those obtained by ASTM method.

The standard deviation of less than 0.05% obtained in our study may point to high precision of the method and possibly, little or no interference(s) in the proposed method. The accuracy of the proposed method was evaluated by direct comparison applied to the same sample using ASTM certified method in Table 1. Coefficients of variation on the order of 7 to 10.8 percent were obtained for all of the analyses except for the very low concentrations.

By varying the pH, this extraction system can be applied to real samples such as extraction from steel samples, sea water and soil (Table 2).

CONCLUSION

From the standpoint of extraction capability, all studied solvents appeared to be very good; enhancing full recoveries of metals from the oil, as all the metal in the colloidal suspensions are atomized. In addition to permitting cheap inorganic standards to be used, the acidic mixed-solvent system has been shown to be effective in standardizing solutions so that systematic errors are obviated. From the practical point of view the proposed method is viable.

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