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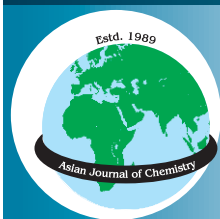


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Analysis of Lubricating Grease by ICP-OES: A Case Study on Preparation Methodology

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The aim of this study was to develop simple, cost effective and reliable sample preparation methods for the analysis of lubricating grease samples. Direct dilution, microwave digestion and emulsification methods were designed and compared for the analysis of Ca, B, Al, Na, Mo, Zn and Ba with inductively coupled plasma optical emission spectroscopy (ICP-OES). The direct dilution method gave most inconsistent results in terms of percentage recovery. The optimized microwave digestion and emulsification methods compared well and showed good reliability in terms of sensitivity and selectivity. The calibration curves resulting from oil emulsion has no significant difference with that of aqueous emulsions, but the stability of the emulsified samples was very low. The limit of detection and limit of quantification values obtained from the microwave digestion method were very low and therefore it is superior amongst the three methods for the analysis of various lubricating grease samples.

Keywords: Lubricating grease, Multi-elemental determination, Emulsification method, ICP-OES.

INTRODUCTION

The fundamental research of grease lubrication is comparatively less in the academic community, presumably due to lack of funding. Grease acts as a mechanical barrier between two moving surfaces serving to keep them apart, leads invariably into the realm of physics [1]. Lubricating grease (LG) possess various kind of advantages in the industrial sector, enhancing the life span of machinery by reducing the friction [2]. The non-biodegradable lubricants cause the environmental pollution [3]. Fourier transformation infra-red spectroscopy (FT-IR) was also employed for lubricating grease to know its degradable property [4]. The basic obligation to monitor the lubricating grease is to determine the elemental composition and basic changes in the nature of grease [5]. The American Society of Testing and Materials (ASTM) along with their European and Japanese counterparts have standardized a vast number of tests to measure a specific or physical property of grease. The analysis of grease film thickness is also important in petroleum industries. Complex greases were developed to improve the heat resistance of soap greases, the most popular being lithium, aluminium, calcium and barium. These greases are similar to regular greases except that the thickeners contain two dissimilar acids (one fatty, one inorganic) which impart high temperature characteristics to the final product. The metal content can also indicate the amount of thickeners in the grease and this can assist in the process of trouble shooting technical

problems with new and used grease [6]. Generally electro-coagulation procedure was used industries to remove the lubricating grease and heavy metals from wastewater [7].

A literature survey reveals that several analytical techniques have been reported for the elemental determination of petroleum and related products. The technique applied for analysis of real samples should be based on the nature of the analyte, matrix and the availability of equipment [8]. Modern analytical instruments were employed to improve the elemental determination in the last few years. However the sample preparation remains a challenge due to it being cumbersome, labor-intensive and time consuming [9]. Although atomic absorption spectrophotometry (AAS) is relatively low-cost and easy handling instrument for the elemental determination, the following problems encountered by consumption of large quantity of sample and also interference effects [10,11]. Even though X-ray fluorescence spectroscopy (XFS) is a sophisticated technique, it does not quantify the important lubricating grease components like lithium and boron in real samples [12]. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) shows slight interference effects depending on the nature of sample [13]. However ICP-OES gives the better results with high specificity, sensitivity and reproducibility. The main objective of the present work was to develop a simple cost effective, reliable and quick sampling methodology for the determination of Ca, B, Al, Na, Mo, Zn and Ba found in lubricating grease samples. The present developed methods

can be useful for the routine analysis of elements in the petrochemical industry.

EXPERIMENTAL

An optima 5300 V with advanced 40 MHz free running RF generator ICP Win Lab software two dimensional CCD array detector was used for the multielemental determination of the lubricant samples and standards. A Milli-Q Plus pure water 113 generating system from Millipore (Bedford, MA, USA) was employed for Milli-Q water production. The wavelengths (nm) for aluminium (308.22; 396.15; 309.27), boron (249.677; 208.889), barium (455.403; 493.41; 223.53), calcium (422.673; 396.85; 315.88), lithium (670.784; 610.36; 460.29), molybdenum (202.03; 281.62), phosphorous (213.62; 214.91; 253.40), sodium (589.595) and zinc (206.200; 206.2; 213.86) were used. The important ICP operating parameters were as follows: Power generator: 1.3 kW, Plasma gas flow: 15 L min⁻¹, Auxiliary gas flow: 0.80 L min⁻¹, Nebulizer gas flow: 0.8 L min⁻¹, Nebulizer type: Glass concentric nebulizer, Spray chamber: Glass cyclonic spray chamber, Torch: Axial high solids, Sample uptake rate: 1.0 mL min⁻¹, Integration time: 10 s, Flush time: 30 s, Replicates: 3.

Milli-Q water was used throughout the study for preparations of standards and sample solutions. All the working reagents were purchased as analytical reagent grade. Nitric acid, hydrochloric acid, sulphuric acid were purchased from Merck, South Africa. The custom made standards (S27 and S28) with concentration of 1000 mg L⁻¹ and multi-elements (Al, Ba, Ca, Li, Na, B, Mo, P, S and Zn) were purchased from Supelco, South Africa. Toluene ≥ 99 % purity, xylene anhydrous ≥ 99 % purity, *t*-octylphenoxypolyethoxyethanol (Triton X-100) and hydrogen peroxide were purchased Sigma Aldrich, South Africa. The oil standard (S21) with multi-elements (B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, Al, Ag, V and Zn) was purchased from Conostan Oil Analysis Standards. Low aromatic white spirits and Shellsol A were supplied by Shell, South Africa and 500 mL internal epoxy lined tin cans were obtained from Nampak, South Africa.

Methods: Sample preparation is the most crucial factor for the analysis of lubricating grease [14]. Three different procedures were employed for the preparation of samples in order to identify the most suitable method and to obtain the accurate analytical results

Direct dilution

Preparation of samples and standards: 5 g of lubricating grease was made up to 100 g with YUBase 4 and contents were thoroughly mixed in Silverson mixer for 8 min. Immediately 2 g of the resulting mixture was made up to 20 g with xylene and kerosene mixture to prevent settling out of the sample.

Individually weighed 0.2 g of S21 were made up to 2 g each with YUBase 4 and then diluted to 20 g with the xylene and kerosene. The resulting sample and standards were subjected to analysis.

Emulsification

Preparation of samples and standards: 5 g of lubricating grease was made up to 100 g with YUBase 4 and the resulting

mixture was thoroughly mixed with a Silverson mixer for 8 min. Then 1 mL of the mixture and 0.5 mL concentrated nitric acid was sonicated for 5 min. Finally, 0.1 mL of Triton X-100 was added and the solution made up to 10 mL under slow and continuous agitation followed by the vigorous shaking for 2 min. The resultant mixture was placed in an ultrasonicator for 5 min.

1 mL of YUBase 4 and 0.5 mL of concentrated HNO₃ were mixed in a 10 mL volumetric flasks and sonicated for 5 min. To this mixture 0.1 mL of Triton X-100 was added followed by serial addition of 0.5-4.0 mL of S21 and S27 standards to make 5.0-40 ppm solutions separately.

Microwave digestion

Preparation of samples and standards: 0.2 g of lubricating grease was transferred into a poly tetrafluoro ethylene (PTFE) digestion vessel. To this vessel 8 mL of reverse aqua-regia was added and subjected to pressure relief digestion process, which is a two stage program. The first stage is 125 W for 15 min and the second stage is 190 W for 15 min. The vessel was allowed to cool for 5 min before removing from the system. The vessel was then kept in an ice bath for 30 min and the samples were now ready for the analysis.

100 ppm of the both S27 and S28 were prepared by measuring 10 mL of each standard which was then made up to 100 mL with 5 % of reverse aqua-regia. Upon serial dilution of each standard, by adding 5.0 mL of cobalt internal standard, the required 10-50 ppm solutions were obtained.

General procedure: 500 mL internal epoxy lined tin cans with screw metal caps were used as grease sample containers. The containers were cleaned initially with warm soap water, then soaked with 10 % HNO₃ and then air dried. Samples were stored in a dry cool cupboard to prevent from degradation from light and heat.

Limit of detection (LOD) and limit of quantification (LOQ) were calculated based on the mean and standard deviation of blank responses. The selectivity and specificity of the method was established with 10 ppm internal standards (S21 and S27) scanned at the selected wavelengths. The reproducibility and RSD's were calculated by six individual determinations of the analyte ranging from 5 to 20 ppm of analyte concentration. The linearity was determined by the average of six consecutive measurements of standard with a range of 0 to 40 mg L⁻¹.

RESULTS AND DISCUSSION

Based on method validation, limit of detection's, limit of quantification's, precision, accuracy and linearity were established. Most of the metal concentrations cannot be calculated theoretically as there is no information on their concentrations in the raw materials. The most prominent metals like Ca, B, Al, Na, Mo, Zn, Ba and Li were determined by the proposed methods.

In the dilution method, white spirit does not adequately dissolve the shear mixed samples. Therefore, reproducible results were not obtained for most of the metals. On the other hand usage of toluene and benzene as solvent mixtures, increases the organic content on the quartz torch and leads to

the plasma destabilization or even plasma extinction. Finally metal free aviation kerosene and xylene solvent combination was dissolved in the shear mixed sample, which resulted in a poor recovery percentages for both Ca and Li metals with their simplex and complexes (Table-1). The alteration in the concentration of the sample causes evaporation of the solvent and as a result deposition of metals on the walls of the container occurred.

TABLE-1
PERCENTAGE OF RECOVERIES OF FOUR DIFFERENT LUBRICANT GREASES OBTAINED IN DILUTION METHOD

Grease type	Inductive metal	Concentration (ppm)		Recovery (%)
		Theoretical	Actual	
Lithium simplex	Li	3516	1160	33.7
Lithium complex	B	2309	969	42.4
Calcium simplex	Ca	1564	797	51.6
Calcium complex	B	2309	715	31.3

The emulsification method adopted in the present study was followed from the reported method [15] with a slight modifications in order to analyse the multi-elements present in the lubricating grease samples. This method was carried out with the addition of Triton X-100, which gave acceptable recoveries and stability in emulsion [16]. However to improve the percentage of recovery, Triton X-100 concentration was varied in the range of 1-10 %. The maximum recovery percentages were observed in the range of 6-10 % with high stability in emulsion (40 min), whereas below 6 %, low recoveries and less stability (17 min) was observed (Table-2). Using the emulsification method, metal free base oil standard samples were analyzed with fair percentages of recovery and detection limits (Tables 3 and 4). In the emulsification method, comparison between aqueous and emulsion standard solutions were also investigated using calibration method with 6 % Triton-X. The slope values obtained from the calibration curves for all the elements Ca, B, Al, Na, Mo, Zn, Ba and Li slightly differs, but not the intercept values (Figs. 1 and 2), which indicated that there was no significant difference in the base line measurements by using either oil or aqueous emulsion.

In the microwave digestion method, poor results were observed without the acid treatment (reverse aqua regia)

TABLE-2
EFFECT OF SURFACTANT TRITON X-100 ON THE STABILITY OF EMULSION MIXTURE

Sample number	Mass percentage of oil sample	Mass percentage (Triton X-100)	Stability (Time, min)
1	5	1	Unstable
2	5	2	Unstable
3	5	3	Unstable
4	5	4	7.0
5	5	5	17.0
6	5	6	40.0
7	5	7	39.5
8	5	8	39.0
9	5	9	39.6
10	5	10	39.4
11	5	15	12.0
12	5	20	10.0

TABLE-3
COMPARATIVE ANALYTICAL DATA OF BOTH EMULSIFICATION AND MICROWAVE METHODS

Element	Correlation coefficient (R ²)	Average % Recovery	RSD (%)	LOD (mg L ⁻¹)	LOQ (mg L ⁻¹)
Emulsification method					
Ca	0.996	101.20	4.20	0.20	0.65
B	0.993	99.20	3.30	0.03	0.47
Al	0.999	100.40	0.80	0.03	0.04
Na	0.999	100.40	0.90	0.04	0.14
Mo	0.996	109.20	1.60	0.09	0.31
Zn	0.998	101.40	3.60	0.15	0.51
Ba	0.994	103.20	4.50	0.09	0.30
Li	0.997	99.90	3.90	0.09	0.31
Microwave method					
Ca	0.996	100.70	1.20	0.14	0.43
B	0.993	100.92	1.01	0.26	0.81
Al	0.999	102.85	0.76	0.10	0.31
Na	0.999	102.20	0.58	0.03	0.09
Mo	0.996	99.47	0.60	0.07	0.23
Zn	0.998	101.87	0.56	0.10	0.33
Ba	0.994	100.34	0.85	0.05	0.16
Li	0.997	100.05	0.74	0.06	0.20

TABLE-4
RECOVERIES OF FOUR DIFFERENT LUBRICANTS OBTAINED IN BOTH EMULSIFICATION AND MICROWAVE METHODS

Grease type	Inductive metal	Concentration (ppm)		Recovery (%)
		Theoretical	Actual	
Emulsification method				
Lithium simplex	Li	3516	3499	99.5
Lithium complex	B	2309	2319	100.4
Calcium simplex	Ca	1564	1583	101.2
Calcium complex	B	2309	2330	100.9
Microwave method				
Lithium simplex	Li	3516	3512	99.4
Lithium complex	B	2309	2274	98.6
Calcium simplex	Ca	1564	1565	100.2
Calcium complex	B	2309	2270	98.6

procedure, due to the inadequate digestion of the sample. Therefore, optimized conditions such as sample amount, concentrated acid volumes, microwave radiation power and digestion time for the acid have been designed. In order to make the sample digestion step rapid, 3:1 mixture of concentrated HNO₃ and HCl (reverse aqua regia) was added [17,18] followed by the addition of hydrogen peroxide, which acts as a clarifying agent. The accurate results with improved recoveries were obtained after optimization of microwave digestion method for four lubricating grease samples (Tables 3 and 4). The low boron recovery in the present study, may be due to the release of gas under high pressure which resulted in loss of the sample (volatile boron).

Conclusion

The results obtained from the direct dilution method was not reproducible with much lower recoveries and in addition the organic solvent content affects the plasma destabilization. In case of the emulsification method, acceptable sensitivity was observed, with minimal matrix effect, which resulted in the achievement of low detection limits when compared to the microwave digestion method. Due to this reason, it is proved

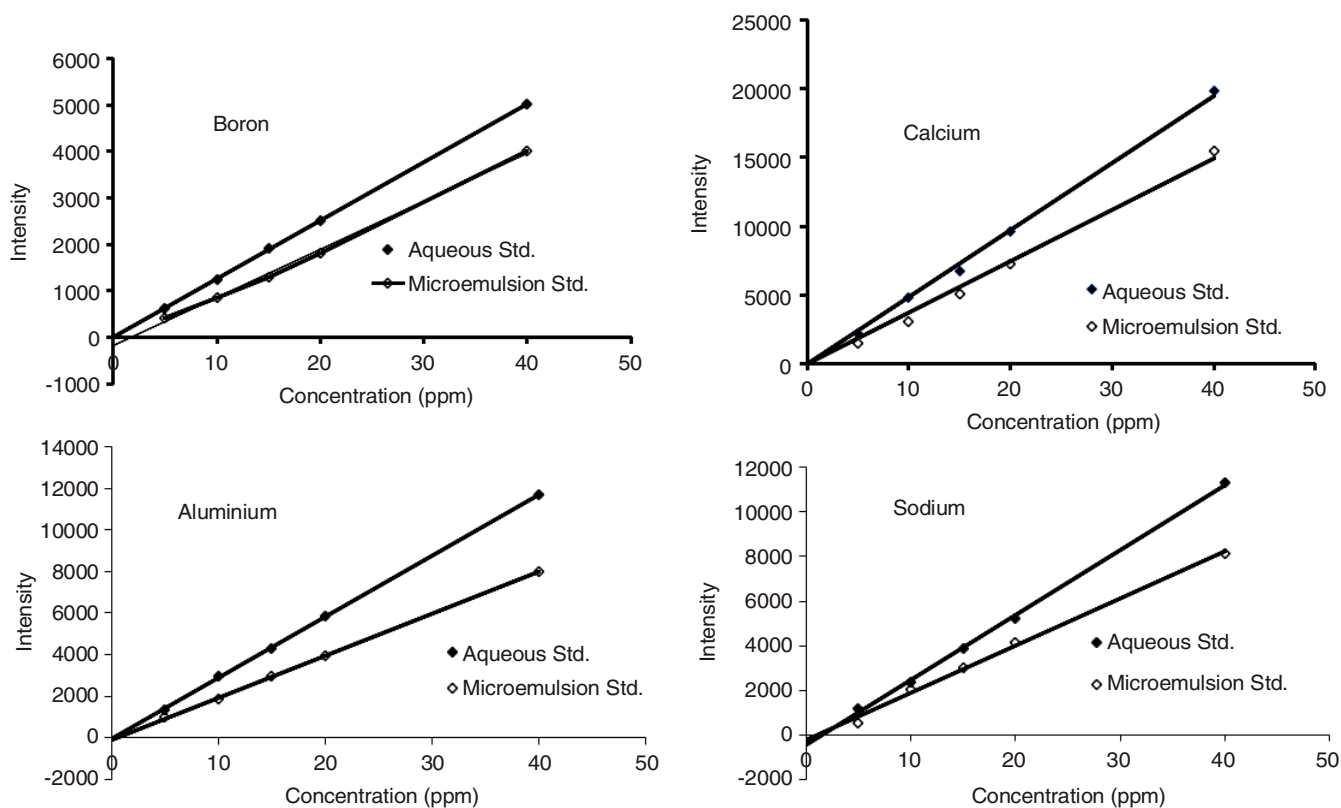


Fig. 1. Calibration plots for boron, calcium, aluminium and sodium prepared in aqueous and in emulsion based oils

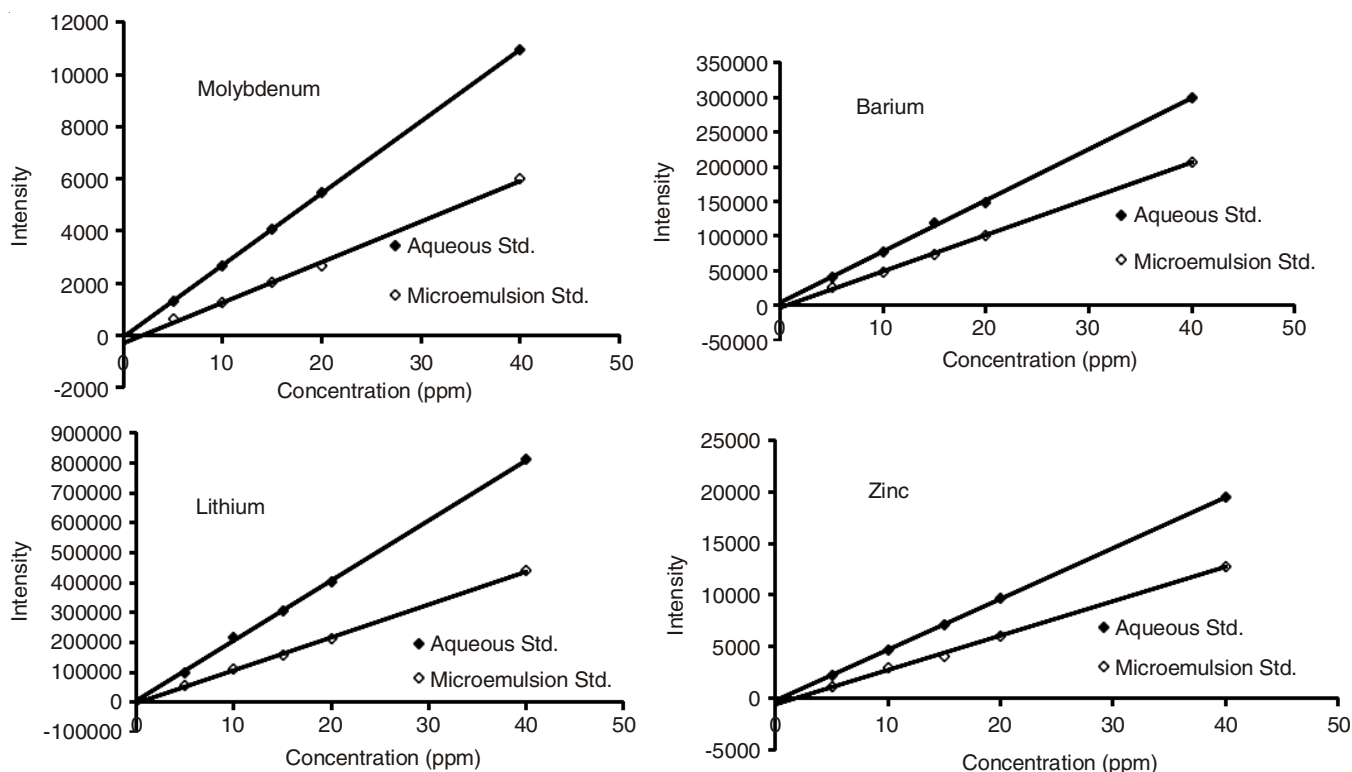


Fig. 2. Calibration plots for molybdenum, barium, lithium and zinc prepared in aqueous and in emulsion based oils

to be an equally efficient method in terms of rapidity with microwave digestion method for routine analysis. A system based on oil-in-water micro emulsion, mainly with a large amount of water, is advantageous in order to reduce the cost because of its similarity to aqueous solutions. However, the

main drawback with this method is the instability of the emulsions. Finally, microwave digestion still remains the most better method for elemental Ca, B, Al, Na, Mo, Zn, Ba and Li determination although it is more time consuming compared to the emulsification method. Despite its sample size

constraints closed vessel microwave digestion offers the benefit of good recovery and precision for analytes that may be volatilized under other decomposition techniques that are open to the atmosphere. Microwave digestion method allows in-process products to be analyzed and corrections can be made before the packaging stage. It also enables an exhaustive product characterization, which may be required by the customers.

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