

An Evaluation of Emulsions in Wear-Metal-in-Oil Analyses

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ABSTRACT

The emulsification of used lubricating oil as a method of sample preparation, preceding the determination of wear-metals in the oil using ICP-OES, was compared to the preparatory methods of ashing and dilution. The oil samples were treated with acid and emulsified in water (1% w/w) using tetralin as a solvent and Triton X-100 as a surfactant. The performance characteristics (detection limits, accuracy, precision and spike recovery) of the emulsion methodology were evaluated. The calibration for the emulsion method compared favourably with the traditional methods of sample preparation. The detection limits for the emulsion method were lower in certain cases than those for ashing and dilution. The precision was on average approximately 2% RSD or less, except where the sample's concentration value was close to the detection limit.

KEYWORDS

Emulsions, wear-metals, lubricating oil, ICP-OES.

1. Introduction

The most widely used techniques for elemental analysis in oil are atomic absorption spectrometry (FAAS and ETAAS)^{1–3} and inductively coupled plasma optical emission spectrometry (ICP-OES).^{4–7} These spectrometric techniques are used because of their high sensitivity and high analysis rate.¹ The predominant problem encountered is the high viscosity of the oil. This creates difficulty in the sample nebulization and has traditionally been overcome by using complex sample and standard preparation.

The following methods have been used in sample preparation to determine metals in oil samples: i) dilution with a suitable organic solvent,^{2–9} ii) removal of the organic matrix by wet oxidation with acid digestion,¹⁰ iii) ashing of the sample prior to analysis,¹¹ iv) extractions¹² and v) heating of the oil sample in order to reduce its viscosity.¹³ The majority of these methods are time-consuming and increase the risk of sample contamination or analyte loss.

Direct dilution methods are not useful for FAAS where the larger particles pass through the flame without being atomized.¹⁴ The presence of different analyte species, together with the differences between the properties of the organic solvents and water, cause difficulty with the signal correlation between aqueous standards and oil samples, even when using a graphite tube atomizer in ETAAS.¹⁵ When using ICP-OES for oil analysis, direct dilution of the sample with white spirits, or a similar solvent, allows for direct aspiration of the sample into the plasma. This method, however, creates carbon deposits on the torch, high noise levels and requires the use of organometallic standards.¹⁶ Organometallic compounds dissolved in purified oil compensate for matrix effects and simplify calibration. The disadvantage of this is that they are relatively expensive and difficult to prepare. The use of organic solvents for dilution introduces the problem of volatility, which in turn affects the analytical signal. Solvents more volatile than water require increased plasma power and plasma gas in order to protect the torch. Oxygen is needed to achieve solvent vapour combustion and to prevent carbon build-up.¹⁷

With digestion treatments the analyte present in the form of

metallic particles is dissolved, and analyte present as organo-metallic species is converted into ions, thus removing many of the matrix affects during analysis. The properties of the samples are then physically and chemically similar to those of aqueous standards and allow for the use of a single calibration curve for various matrices.¹⁸ The disadvantages include the laborious and time-consuming sample preparation as well as trace metal contamination from acid reagents, digestion vessels and dust particles.

Ashing with subsequent acid dissolution is time-consuming and requires many steps, which increase the risk of analyte contamination or loss.

Noise, sensitivity fluctuations and characteristic flame problems have all necessitated the need for an alternative approach¹⁹ to sample preparation in oil analysis. Direct emulsification of the oil samples with surfactants provides a rapid methodology for sample preparation without the destruction of organic matter.²⁰ This method is not time-consuming, reduces viscosity and decreases the organic content of the sample solution by 96%.²¹ For oil-in-water microemulsions the oil is evenly dispersed in the water phase thereby making the properties of the emulsion similar to those of an aqueous solution. The use of aqueous calibration standard solutions simplifies the emulsion methodology, thereby making it inexpensive and accurate. The only requirement for this methodology is that the emulsions must be stable and thus the use of a suitable surfactant is important.¹⁹ This infers to the selection of a surfactant with a suitable HLB (hydrophilic-lipophilic balance) for stabilization.

The analytical applications of emulsions have included the determination of lead in gasoline by AAS based on the formation of stable oil-in-water emulsions.^{22,23} AAS has also been used for the determination of nickel in fuel oil using water-in-oil emulsions with Renex 690 as the emulsifier.²⁴ The metal content of lubricating oils are routinely determined as the presence of certain metals in used oil serves as important indicators in the maintenance strategy of machines. These metallic elements include iron, aluminium and nickel, which are present due to the wear of the engine and turbine components. Cr, Cu, Pb, Mg and Si have also been determined to this extent using AAS.¹⁹

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The motivation for this study stems from the fact that emulsion methodology has not been widely used in industry in spite of the aforementioned advantages. An attempt was made here to directly compare different variations of this emulsification methodology with the more common methods of ashing and dilution with an organic solvent (xylene). Emulsions were used in the determination of wear metals (Al, Cr, Cu, Fe, Ni and Pb) in used lubricating oil using ICP-OES.

2. Experimental

2.1. Instrumentation

A Varian Liberty 110 Inductively Coupled Plasma Optical Emission Spectrometer, equipped with a sequential monochromator and Babington V-groove nebulizer, was used. The standard argon humidifier in the nebulizer gas line was disconnected for the dilution method in order to prevent the formation of an emulsion in the nebulizer and spray chamber. The conventional Sturman-Masters spray chamber and standard one-piece torch were used for the ashing, dilution, and oil-in-water emulsification analyses.

2.2. Reagents

2.2.1. Samples

Used lubricating oil (Castrol GTX 20W50, Castrol, South Africa) and unused lubricating oil (Castrol GTX 20W50) were used as samples. The used oil was drained from a car engine during a routine service at a garage.

2.2.2. Standards

Aqueous standards prepared from a 1000 $\mu\text{g mL}^{-1}$ multielement stock solution (ICP Multielement IV, Merck, Darmstadt), diluted with deionized water and acidified with concentrated nitric acid were used for the ashing study. All acids used were of Analytical Reagent (A.R.) grade (Merck, Darmstadt).

A 900 $\mu\text{g g}^{-1}$ Conostan S-12 Organometallic Standard (Conostan, Milwaukee) was used as the stock from which the spiked samples and standards were prepared in the dilution study. Base oil 75 (Conostan) was used to prepare the calibration standards and A.R. grade xylene (Associated Chemical Enterprises, South Africa) was used as solvent.

Unused Castrol GTX was used to prepare the emulsified calibration standards. The same Conostan S-12 oil standard was used to prepare the oil emulsion calibration standards. The aqueous stock solution used in the ashing calibration was used to prepare the aqueous emulsion calibration standards. Tetralin (Fluka, Steinheim) was used as solvent and Triton X-100 (BDH Chemicals, Poole) as surfactant.

2.3. Method

2.3.1. Ashing

Aqueous standards were used to prepare the following calibration series: 0, 1, 5 and 9 $\mu\text{g mL}^{-1}$. An extended calibration was used for the lead samples (0, 1, 5, 9, 20, 50 and 100 $\mu\text{g mL}^{-1}$). The nitric acid content of the standards was similar to that of the samples as described below.

The oil sample preparation began with triplicate samples, of 1 g each, being accurately weighed for each type of oil into porcelain crucibles. The porcelain crucibles, in which the oils were weighed, were covered and placed in an oven for 2 hours at 120°C. 1 mL concentrated sulphuric acid was added to aid charring. The temperature was gradually raised and heating

continued until 220°C. The crucibles were placed in a muffle furnace at 220°C and the heating process continued. The crucibles were subsequently heated for 1 hour at 350°C. The temperature was raised in 50°C steps maintaining each step for 30 minutes. Finally the oils were ashed at 600°C for 4 hours and left to cool.²⁵ The cooled ash was dissolved in 5 mL concentrated nitric acid and quantitatively transferred to 50 mL volumetric flasks, which were made up to volume with deionized water.

From each of the used and unused oil samples prepared as described above, three 5 mL aliquots were taken. The first was diluted to 50 mL with deionized water, while the second and third aliquots were spiked with aqueous standard to contain 1 $\mu\text{g mL}^{-1}$ and 5 $\mu\text{g mL}^{-1}$ of analyte, respectively.

2.3.2. Dilution with Xylene

The oil standard and base oil were diluted with xylene and used to prepare the following calibration series: 0, 1, 5 and 10 $\mu\text{g mL}^{-1}$. For lead an extended calibration series was prepared: 0, 1, 5, 10, 20 and 50 $\mu\text{g mL}^{-1}$. Calibration standards were prepared using the Conostan base oil 75. The base oil was added to the blank, standards and samples to achieve a 10% w/v total oil content.²⁶

In the sample preparation, 5 g of lubricating oil (used and unused) was accurately weighed and shaken in an ultrasonic bath for 5 minutes and then diluted with xylene to 50 mL (1/10 w/v). Spiked samples were prepared in a similar manner by adding the Conostan S-12 organometallic oil standard to the oil.

2.3.3. Oil-in-water Emulsification

Three different calibration standard series were used for the emulsification method: an oil emulsion series, an aqueous emulsion series and an aqueous series.

The oil emulsion calibration standards were prepared by adding the oil standard as part of the oil phase. 0.5 g in total of the unused lubricating oil and oil standard was accurately weighed in an Erlenmeyer flask and treated with 2.5 mL concentrated nitric acid for 5 minutes in an ultrasonic bath. 0.5 g of tetralin was then added and the mixture mixed for a few minutes. 1.0 g of triton X-100 was added and sonication continued for 5 minutes. The deionized water was added until a final mass of 50 g was obtained. The following calibration series was prepared: 0, 1, 5 and 9 $\mu\text{g g}^{-1}$ emulsion.

The aqueous emulsion calibration standards were prepared by adding the aqueous standard as part of the aqueous phase to the emulsified oil (acid-treated) and the following calibration series was prepared: 0, 1, 5 and 9 $\mu\text{g g}^{-1}$ emulsion.

The aqueous calibration standards were prepared by diluting the aqueous stock solution with deionized water and concentrated nitric acid (a similar concentration to that in the emulsions) to obtain the following calibration series: 0, 1, 5 and 9 $\mu\text{g mL}^{-1}$.

The sample preparation was similar to that of the emulsified calibration standards except that the used lubricating oil was used. Spiked samples (1 and 5 $\mu\text{g g}^{-1}$ emulsion) were prepared by adding the Conostan S-12 organometallic oil standard to the oil phase prior to the acid treatment.

2.4. Analytical Wavelengths

The common analytical wavelengths utilized for the methods are presented in Table 1.

2.5. Optimized Working Conditions

The operating conditions were optimized for the emulsification, ashing and dilution methods and are presented in Tables 2 and 3.

Table 1 Analytical wavelengths used.

Element	Wavelengths /nm
Al (I)	396.152
Cr (II)	283.563
Cu (I)	324.754
Fe (II)	259.940
Ni (I)	352.454 ^a
Pb (II)	220.353

^a The 231.604nm Ni (II) line was used in the dilution study

3. Results and Discussion

3.1. Emulsion Characterization

The emulsions prepared were of an opaque yellow colour and underwent phase separation after several hours. The emulsions could be reconstituted, however, by vortexing them for at least a minute. Based on these observations, the emulsions prepared should be classified as macroemulsions.²⁷

3.2. Comparison of Calibrations

The calibration range was limited due to dilution constraints imposed by the Conostan S-12 oil standard used in the oil emulsion calibration preparation. This limited range was kept for each of the method calibrations for comparative reasons.

The calibration data for the different methods are presented in Table 4. The three emulsification methods resulted in similar sensitivities on all of the elements as determined by the calibration curves. The linearity of each of the calibrations over the limited range was excellent. Excellent linear correlation was also found for the calibrations of the ashed oil. The sensitivity was lower than that for the emulsification methods while the regression coefficients were similar. The linearity was very good and the sensitivity was higher, for the dilution method, than those found for the ashing and emulsification methods.

Table 4 Linear regression equations obtained for each of the methods.

	Aqueous emulsion	Oil emulsion	Aqueous	Ashing	Dilution
Al					
Slope	3810.4	3532.4	3714.7	3335.5	6503.4
Intercept	-119.51	-229.7	70.995	215.54	5014.8
R ²	0.9999	0.9996	0.9995	0.9975	0.9999
Cr					
Slope	6893.3	6020.5	5641	3889.2	14823
Intercept	-42.919	-405.28	-196.98	88.901	965.4
R ²	1	0.9997	0.9970	0.9999	0.9998
Cu					
Slope	4702.1	4288.2	3550.1	3073.9	8846.1
Intercept	-52.739	-200.82	-136.52	129.23	1068
R ²	1	0.9999	0.9955	0.9999	0.9987
Fe					
Slope	16692	15943	13582	10083	23592
Intercept	371.18	-861.28	82.699	255.44	1075.7
R ²	1	0.9996	0.9999	0.9996	0.9999
Ni					
Slope	2514.7	2448.3	2192.8	1655.7	14681
Intercept	10.78	-107.44	185.98	245.06	-548.34
R ²	0.9999	0.9999	0.9999	0.9930	0.9999
Pb					
Slope	1819.3	1573.2	1884.4	1239.9	2940.3
Intercept	62.038	-33.701	34.026	-610.38	605.61
R ²	1	0.9995	0.9982	0.9990	1

Table 2 Optimized working conditions for ICP-OES determination following ashing or oil-in-water emulsification.

Plasma gas flow /L min ⁻¹	16.5					
Auxiliary gas flow /L min ⁻¹	1.5					
Sample uptake rate /mL min ⁻¹	2.8					
Nebulizer pressure /kPa	150					
	Al	Cr	Cu	Fe	Ni	Pb
Viewing height /mm	2	5	4	6	8	8
Plasma power /kW	1	1.2	1.2	1.2	1	1.2

Table 3 Optimized working conditions for dilution with xylene as solvent.

Plasma gas flow /L min ⁻¹	15					
Auxiliary gas flow /L min ⁻¹	2.25					
Sample uptake rate /mL min ⁻¹	1.8					
Nebulizer pressure /kPa	100					
Plasma power /kW	1.5					
	Al	Cr	Cu	Fe	Ni	Pb
Viewing height /mm	15	7	9	12	9	12

3.3. Detection Limits

The detection limits were based on two different methods: 1) $DL = s_B + 3\sigma_B$ where B refers blank measurements, and 2) Meier and Zünd's method,²⁸ which is a calibration curve based calculation. The detection limits of the reference methods as well as the emulsification methods are compared in Table 5. When the 3σ determination was unreliable (i.e. it yielded negative results), the Meier and Zünd value was taken as the accepted detection limit. The Meier and Zünd values were used exclusively for the dilution method and were always higher than the 3σ values. The

Table 5 Comparison of detection limits / $\mu\text{g g}^{-1}$ oil.

Element	Ashing		Dilution		Aqueous emulsion		Oil emulsion		Aqueous	
	3σ	MZ ^a	3σ	MZ	3σ	MZ	3σ	MZ	3σ	MZ
Al	1	39	-0.3	2	5	17	9	39	4	35
Cr	2	8	-0.6	2	2	93	12	35	8	89
Cu	-1	9	-1	6	3	11	6	22	9	108
Fe	0.4	15	-0.4	1	-0.3	8	7	37	0.1	15
Ni	-5	66	-0.2	2	4	13	10	24	-1	19
Pb	28	125	0.4	0.9	5	6	8	38	1	37

^a Calculated according to the method of Meier and Zund.²⁷

Meier and Zünd method can therefore be regarded as a practical detection limit.

3.4. Accuracy and Precision

The oil samples were treated with a small amount of concentrated nitric acid to reduce the size of any large metallic particles potentially present in order to determine the total elemental concentration for the emulsification methods.

The concentrations, the standard deviations ($n = 3$) and %RSD values for the used oil are presented in Table 6. The variations in the concentration values could generally be ascribed to the execution of the reference and emulsification methods over a few months and not a few days. In cases where a negative concentration value was obtained the lettering 'nd' is ascribed meaning that those values were 'not determined' after background correction was applied.

The statistical comparisons were performed at the 95% confidence level. The ashing method's concentration value obtained

for aluminium was statistically different from the value obtained using the emulsification methods. The aqueous emulsion and aqueous calibration methods showed no statistical difference, but were statistically different from the oil emulsion calibration value for aluminium. The aqueous emulsion and aqueous calibration values were approximately $10 \mu\text{g g}^{-1}$ oil, and the oil emulsion value was approximately $15 \mu\text{g g}^{-1}$ oil. Although these values were of the same order of magnitude, no conclusion can be made concerning the accuracy of the aluminium determination from these results. The levels found for the emulsification methods fall approximately in the expected range for an used lubricating oil. The low levels found for ashing indicate the probability of analyte loss with the formation of soot during ashing. There is no clear explanation available as to why the dilution method yielded low results apart from a hypothesis that the higher plasma loading due to the organic matrix, led to incomplete atomization of refractory Al_2O_3 . This qualitative basis indicates that the emulsification and aqueous methods are more

Table 6 Comparison of concentration values for elements analysed in used lubricating oil.

Element	Ashing	Dilution	Emulsification		Aqueous
			Aqueous emulsion	Oil emulsion	
Al					
Avg. conc. / $\mu\text{g g}^{-1}$ oil	2	nd	9.9	14.9	9.9
S	1.1	-	0.87	0.23	0.45
%RSD	63	-	8.8	1.5	4.5
Cr					
Avg. conc. / $\mu\text{g g}^{-1}$ oil	6	5.15	6.8	14.0	10.9
S	1.4	0.044	0.18	0.45	0.12
%RSD	22	0.85	2.7	3.2	1.1
Cu					
Avg. conc. / $\mu\text{g g}^{-1}$ oil	<9	<6	9.5	13.5	14.3
S	-	-	0.24	0.29	0.33
%RSD	-	-	2.5	2.1	2.3
Fe					
Avg. conc. / $\mu\text{g g}^{-1}$ oil	23.7	23.42	21.6	32.1	29.4
S	0.24	0.089	0.18	0.26	0.57
%RSD	1.0	0.38	0.83	0.80	2.0
Ni					
Avg. conc. / $\mu\text{g g}^{-1}$ oil	nd	<2	≤ 4	<10	nd
S	-	-	-	-	-
%RSD	-	-	-	-	-
Pb					
Avg. conc. ^a / mg g^{-1} oil	3.71	3.57	3.89	4.19	3.54
S	0.021	0.024	0.023	0.034	0.038
%RSD	0.56	0.67	0.58	0.81	1.1
Avg. conc. $10\times$ dilution ^b / mg g^{-1} oil	-	3.559	3.61	4.03	4.00
S	-	0.0086	0.035	0.031	0.049
%RSD	-	0.24	0.96	0.77	1.2

^a Values extrapolated on calibration curve before sample was diluted.

^b Values obtained after sample was diluted ten times with clean oil.

reliable than the ashing method for aluminium determination.

The reference values obtained for the ashing and dilution methods were found to have no significant difference for chromium. The aqueous emulsion calibration value was found to have no significant difference to the ashing value but was significantly different from the dilution value.

The copper concentration fell below that of the detection limit and thus was of no practical use in the comparison of the methods. The comparison of the emulsification values showed a significant difference amongst the three calibration methods. Their 3σ detection limits (Table 5) were of the same order of magnitude with the aqueous calibration having the highest 3σ detection limit and concentration value.

The reference values obtained for iron, from the dilution and ashing methods were not significantly different, unlike the value obtained from the aqueous emulsion calibration. The oil emulsion calibration yielded the highest 3σ detection limit and corresponding high concentration value for iron. When compared to the other methods, the aqueous calibration gave similar values but a poorer precision.

Due to the extremely low nickel content in the oil sample, no comparisons could be made between the methods. The concentration determined using the aqueous emulsion calibration ($4.044 \mu\text{g g}^{-1}$ oil) was very close to the accepted detection limit ($4 \mu\text{g g}^{-1}$ oil). Thus this value cannot be accepted as the true value.

The lead level of the used oil sample was very high. Table 6 shows the initial run where the average concentration values for the dilution and emulsification methods were extrapolated from the regression lines of the calibration graphs. Thereafter the used oil sample was diluted 10 times with unused oil in order to facilitate the calibration for lead. The only reference method that was applied to the 10 times diluted sample was that of dilution. Comparing dilution to the three emulsification methods, it was found that the aqueous emulsion method and aqueous calibration method gave concentration values that were not significantly different from the dilution method's. The high concentration of lead in the used oil corroborated the garage's theory that leaded petrol had come into contact with the car's oil supply.

In all cases, the oil emulsion calibration yielded the highest concentration values, whereas the dilution method yielded lower values, even though the same Conostan oil standard was used. The limited shelf-life of oil standards (12 months) indicates that aqueous standards would be a more practical option.

The standard deviations (s) for all the methods used to determine the metal content in the used oil were comparable. The precision for the dilution method for all the elements analysed was less than 1% RSD. The ashing method exhibited poor precision especially for elements such as aluminium and chromium (63 and 22%, respectively). The precision obtained, for lead and iron, for the emulsification method was found to be comparable to that of the dilution method. Absolute accuracy, although desirable, is not of such critical importance when the method is to be used for routine analyses where the relative changes in concentration are of greater importance. The standard deviations were based on 3 replicate measurements. Although this represents a small sample population, it is still useful for comparative purposes. An increase in the number of measurements would require an increase in the time, cost and the amount of sample used in the analysis, resulting in added demands put on an already limited sample amount.

Only ashing and dilution were used to determine the elemental content of the unused oil, because unused oil was used to prepare the emulsified calibration standards. The concentra-

tions were found to be either below or close to the detection limit. Thus the unused oil was free of any detectable elements that were to be analysed for in the used oil. The suitability of the unused oil for use in the preparation of emulsified calibration standards, as a cheaper alternative was verified. The standard deviation and %RSD values for the unused oil were very high in the cases of aluminium, iron and lead, therefore the concentration values obtained cannot be accepted as precise or accurate with absolute certainty. The detection limits for aluminium, iron and lead were 1, 0.4 and $28 \mu\text{g g}^{-1}$ oil, respectively, for the ashing method and the concentration values were all close to this limit. Lead, for which the ashing method value for the unused oil was found to be $36.6 \pm 8 \mu\text{g g}^{-1}$ oil, can be present in unused oil as an organic lead compound used to minimize wear. Bias is indicated in the ashing method for the lead determination because of the high %RSD. The lead content for the dilution method is similar to the standard deviation, but well above the detection limit, indicating better reliability of the method.

The methods were also evaluated with regards to preparation and analysis time, practicality of the method as well as instrumental demands. The ashing method exhibited the following problems: long ashing times (up to ten hours) were needed, and the operator's attention was required to manually increase the temperature ramps to avoid sputtering caused by rapid heating. The unused oil, when ashed in the same manner as the used oil, formed a black ash residue that did not fully dissolve in the nitric acid before the transfer step was executed. The quantitative transfer of the ash, from the crucible to the volumetric flask, increased the risk of contamination, and there was always the risk of the formation of insoluble oxides during the ashing step. To remove any particulate matter after the acid dissolution of the ash, the sample was filtered through $0.22 \mu\text{m}$ filter paper. Losses were expected due to the inclusion of this extra preparatory step. The ashing method advantageously required very little apparatus and only aqueous standards.

The dilution method increased background noise levels during the analysis, because of the high level of xylene needed to dilute the oil. The dilution method was found to be less time-consuming, in terms of preparation, than either the ashing or emulsification methods. The organic matrix was dissociated with the use of higher plasma power levels of 1.5 kW. Memory effects were observed for elements such as nickel and iron, longer rinse times were needed so that no signal enhancement, especially in the blank, would occur when taking measurements for the determination of the 3σ detection limit and the sample analysis. Spectral overlap and background shifts are possible interferences when the dilution method is utilized. The background shifts affect the low concentration determinations and dynamic background correction was used in order to avoid them. Analytical element lines were chosen such that spectral interferences were minimal as recommended by the instrument manual. Carbon build-up on the torch, as occurred under the recommended conditions, was probably due to plasma instability and incomplete pyrolysis, this led to degradation in the detection limit.

The emulsification method did not require the long sample preparation time inherent to the ashing method. Sample preparation took between 15–20 minutes per sample and the longest steps were the actual weighing of the small quantities of oil standard required for the calibration emulsions and the acid-treatment. The analysis time was similar to that for aqueous calibrations and no time-consuming clean up was needed, as in the case of the dilution method.

The effect of transport interferences can be identified by the

Table 7 Recovery studies for the ashing, dilution and emulsification methods using used lubricating oil.

Element	Ashing spike concentration / $\mu\text{g g}^{-1}$ oil	Ashing % recovery	Dilution spike concentration / $\mu\text{g g}^{-1}$ oil	Dilution % recovery	Emulsification spike concentration / $\mu\text{g g}^{-1}$ oil	Aqueous emulsion % recovery	Oil emulsion % recovery	Aqueous % recovery
Al	50	104	10	108	100	90	99	72
	250	110	50	97	500	88	99	81
Cr	50	111	10	99	100	85	98	100
	250	120	50	95	500	90	104	91
Cu	50	107	10	87	100	94	107	111
	250	117	50	86	500	92	104	112
Fe	50	116	10	85	100	95	104	124
	250	114	50	95	500	92	102	121
Ni	50	96	10	98	100	98	101	105
	250	104	50	99	500	91	98	106
Pb	50	99	10	N/R	100	N/R	N/R	N/R
	250	77	50	N/R	500	N/R	N/R	N/R
Pb 10 \times dilution	–	–	10	N/R	100	56	70	79
	–	–	50	0	500	47	57	55

N/R = spike not recovered at all.

use of the recovery test. If the physical properties of the sample solution differ significantly from those of the calibration standards then the rate of generation and transport of the appropriately sized aerosol droplets to the plasma may vary. Calibrating the emulsified oil sample with aqueous standards could introduce such interferences because of the differences in viscosity, density and/or surface tension.

Table 7 shows the percentage recovery found when the ashing, dilution and emulsification methods were applied to the used oil.

The recovery studies presented in Table 7, comparing each of the methods used, show a tendency of the ashing method to recover more than was added to the used oil sample and the dilution method to recover less. The recoveries were better for the three emulsification methods than those for the dilution method. The aqueous emulsion calibration was generally the most reliable method, of all the emulsification methods, based on the recovery results. The lead recovery determination was problematic in that the instrument failed to detect the successive increases in analyte concentration for the dilution and emulsification methods. The same trend persisted for the ten times dilution of the used oil sample. In this case the spike concentrations were unfortunately above the calibration range. No recoveries were made in the case of the dilution method, while the three emulsification methods only partially recovered the lead analyte. The organic matrix was destroyed in the ashing method, while the dilution and emulsification methods merely

diluted it. Thus transport interference effects or volatilization loss problems were not the major factors affecting the recovery.

An hypothesis was then proposed that the lead was present in an insoluble form, to test this theory an oil-soluble copper standard was required. This standard was not commercially available in the desired concentration and no literature was available to prepare such a copper standard in the laboratory. It was theorized that the insoluble lead would be present in the form of PbS and thereby using a copper standard, the CuS that would form in the same concentration range as the lead would also be insoluble i.e. $K_{sp}(\text{CuS}) = 8 \times 10^{-37}$ and $K_{sp}(\text{PbS}) = 3 \times 10^{-28}$. Increasing copper additions in the aqueous phase were made, with the 1000 $\mu\text{g mL}^{-1}$ copper ICP standard. The concentration and recoveries should have decreased but this was not the case. The use of the aqueous standard did not corroborate this assumption, the recoveries and concentrations were found to be similar to the amount of analyte added. This led to the conclusion that the problem was indeed oil based and some sedimentation was found in the original oil sample container. Precautions such as sonication of the oil before diluting or emulsifying it obviously did nothing to eradicate this problem; neither did the acid treatment used for the emulsification method. The destruction of the organic matrix would be the only likely solution but this is not recommended in a method such as ashing for a volatile element such as lead.²⁵

The recovery study, presented in Table 8, for the unused oil

Table 8 Recovery studies for ashing and dilution using unused lubricating oil.

Element	Ashing spike concentration / $\mu\text{g g}^{-1}$ oil	Ashing % recovery	Dilution spike concentration / $\mu\text{g g}^{-1}$ oil	Dilution % recovery
Al	50	102	10	96
	250	100	50	91
Cr	50	105	10	91
	250	101	50	91
Cu	50	105	10	105
	250	103	50	106
Fe	50	106	10	90
	250	103	50	88
Ni	50	102	10	85
	250	100	50	86
Pb	50	115	10	92
	250	104	50	86

showed satisfactory results for both the ashing and dilution methods. This is an indication that the method and operating conditions are not at fault but rather the sample matrix, which caused the interference problems. Another possibility is that at low concentrations of lead, the method gives satisfactory results while at higher concentrations, as found in the oil sample, it is a matrix effect that causes problems with the recoveries.

4. Conclusions

The emulsification methods compared well with the reference methods of ashing and dilution. Linear calibration curves were obtained and the detection limits were in most cases lower than those obtained for the reference methods. The aqueous emulsion method is the most cost-efficient and suitable choice as an alternative method, with the use of little organic matrix in comparison to the dilution and oil emulsion calibration methods. The aqueous calibration method was biased in that the recoveries obtained were overestimated and the sensitivity was lower than that of the aqueous emulsion calibration. The oil emulsion calibration required the use of the Conostan oil standard, which was far more expensive than the aqueous standard. The process of weighing such small masses of the oil standard with subsequent emulsification was longer. The emulsification method is also far less time-consuming than the ashing method and does not introduce the contamination caused by the crucibles. Despite the lack of conclusive results for lead, overall the emulsification method is more reliable than the reference methods. The acid-treatment of the oil sample reduced the sample's particle size; this improved the efficiency of the method to determine total wear metal content. Such an acid-treatment does not occur in the common dilution method thus the larger particles are passed to waste, undetected by the spectrometer. Macroemulsions thus have a role to play in the future of oil analysis, where it is acceptable for such an emulsion to be reconstituted by vortexing it after phase separation has occurred. The emulsification method is also beneficial for routine analysis in industrial laboratories where the emphasis is on the reduction of analysis cost while producing reliable results.

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