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Method validation of Cd (II) determination in lubrication oil by direct dilution method using atomic absorption spectrophotometer

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Abstract. The research about method validation of Cd (II) determination in lubricating oil by direct dilution method using atomic absorption spectrophotometer (AAS) has been conducted. The optimum parameters such as determination of optimum conditions of solvent and the analytical performance method were performed. The results of the measurement showed good result with the linearity value ($R^2 \geq 0.995$), the limit of detection (LOD) was 0.2209 ppm and limit of quantification (LOQ) was 0.7365 ppm, IDL was 0.0622 ppm and MDL was 0.0346 ppm, repeatability and reproducibility are shown as % RSD < 2/3 CV Horwitz values and the accuracy of this method was well shown by a recovery percentage of 91.65%. Based on the result of research, the direct dilution technique can be used for the determination of Cd (II) in lubrication oil using the AAS method with valid results.

1. Introduction

Lubricant is a material introduced to a system to reduce friction between surfaces in mutual contact in order to minimise heat formation when the surfaces move and provide a protection medium to carry loads (pressure generated) between opposing surface [1]. Lubrication oil is included in the most important parts of the machine. Engine and turbine components undergo continual wear under normal operating conditions. Lubricating oil is used to minimize the wear and friction on metal surfaces that come into contact with one layer of thin film between the two metals, and corrosion [2, 3]. To maintain the components of the engine that rub against each other so that it can have a good function, the type of lubricating oil must be selected that is suitable and needed by the machine. One of the constituent elements in lubricating oil that is very concerned is the content of heavy metals, because many of these metals are potentially very dangerous for living organisms [4]. This metal is sourced from fuel and engine wear.

There are several heavy metal elements which are usually in lubricating oil including such as iron (Fe), chromium (Cr), aluminum (Al), lead (Pb) and cadmium (Cd) may indicate engine wear or any compartment containing lubricating oil [5]. The metal concentration in the lubricating oil increases with the engine operating time, the amount depends on the type of fuel source and the mechanical condition of the engine. Degradation of metals from additives such as calcium (Ca), phosphorus (P) and zinc (Zn) causes variation in rheological properties of lubricant [5]. The greater the metal content in the lubricating oil will inhibit engine performance.



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One of the heavy metals is cadmium (Cd) which is a group of metals with a high level of toxicity after Hg will greatly affect environmental pollution if the level has exceeded the quality standard range. Cd content in oil is < 1 mg/kg, although in a small concentration the metal is expected not to interfere with the performance of the machine [2]. Considering that the use of lubricating oil is important, it is necessary to test the quality and method so as to provide valid analysis results. Therefore, there is a need to control the validated method and the level of heavy metal content in the oil, in order to minimize its influence on the performance of industrial machinery [6].

In this study, a direct dilution method was used to determine Cd in lubricating oil, by dissolving the sample directly using organic solvents. The advantage of this method is that organic solvents used to dissolve lubricant oil samples are fewer, the analysis time is faster when compared to other dilution methods, and the effectiveness is better in routine analysis [7].

Based on the description above, it is necessary to conduct research on method validation of Cd(II) determination in lubricating oil by direct dilution method. The stages of research include solvent optimization tests, determination of several analytic performance parameters, such as linearity, LOD (limit of detection), LOQ (limit of quantification), MDL (Method Detection limit), IDL (instrument detection limit), accuracy and precision of the lubricating oil samples used).

2. Material and methods

2.1. Material

Equipment used in this research were beaker glass, pipette, analytical balance, Erlenmeyer flask, magnetic stirrer, Atomic Absorption Spectrophotometer Varian 240 FS, and hollow cathode lamp of Cd. The materials used in this study include oil blank solution, Cd standard, n-hexane, thinner solution, methyl isobutyl ketone (MIBK) and aquabidest.

2.2. Methods

2.2.1. Preparation of blank solution. Amount of 10 mL of oil blank was put into a measuring flask with a volume of 100 mL, diluted using MIBK solvents and homogenized.

2.2.2. Preparation of standard Cd solution. Five volumetric flasks with a volume of 25 mL were prepared. The standard solution of Cd 50 ppm oil was piped 0.25; 0.5; 1; 2; and 4 mL were then put into a prepared flask. Each measuring flask was diluted using a MIBK solvent and homogenized to obtain a standard solution of Cd with a concentration of 0.5; 1; 2; 4; and 8 ppm, respectively.

2.2.3. Preparation of sample solution. Amount of 2 mL of the lubrication oil sample was put into a 50 mL volumetric flask, diluted lubrication oil samples using MIBK, and homogenized.

2.2.4. Preparation of spike solution. Amount of 1 mL of standard solution of 50 ppm Cd metal oil was put into a volumetric flask as a spike solution for accuracy testing and as much as 1 mL of standard 9 ppm Cd solution was put into another measuring flask as a spike solution for the MDL test. Each solution was diluted using a sample solution and homogenized [8].

2.2.5. Determination of optimum solvent. A total of 6 volumetric flasks with a volume of 50 mL were prepared. Amount of 1 mL and 0.5 mL standard solutions of metal oil Cd 50 ppm were put into each prepared flask and diluted each measuring flask using n-hexane, thinner and MIBK solvents. Absorbance readings for each solvent were carried out using an atomic absorption spectrophotometer.

2.2.6. Linearity test. Blank solution and standard of series solution 0.5–8.0 ppm were prepared. The absorbance of each solution was measured using AAS. The concentration and absorbance values were recorded. Based on the data, the concentration of Cd standard –vs- absorbance curve and a linear line equation was obtained.

2.2.7. *Accuracy test.* Spike solutions and samples that has been prepared in advance were prepared. The absorbance of each solution was measured by using AAS. The absorbance readings and concentrations in each solution were carried out 10 times.

$$\% \text{ Recovery} = \frac{(C_F - C_A)}{C_A} \times 100 \quad (1)$$

Where C_F is total sample concentration from the measurements, C_A is actual sample concentration and C^*_A is the concentration of the analyte added.

2.2.8. *Precision test.* Sample solutions that have been prepared in advance were prepared. The absorbance of the sample solution was measured by using AAS. The absorbance readings and concentrations in each solution were carried out 10 times. The results obtained were recorded. The same procedure was carried out for the 2nd day measurement.

2.2.9. *Limit of Detection (LOD) test.* LOD test have been done statistically through linear regression lines obtained from the calibration curve. Instrument response y is linearly related to x concentration. The detection limit is generally expressed in $3Sa / b$, where b is the slope and SD is the standard deviation.

$$\text{LOD} = 3 \times \text{SD}/b \quad (2)$$

2.2.10. *Limit of Quantity (LOQ) test.* LOQ test have been done statistically through linear regression lines obtained from the calibration curve. Instrument response y is linearly related to x concentration. The detection limit is generally expressed in $10Sa / b$, where b is the slope and SD is the standard deviation [9].

$$\text{LOQ} = 10 \text{SD}/b \quad (3)$$

2.2.11. *Instrument Detection Limit (IDL) and Method Detection Limit (MDL) test.* A blank solution was prepared which has been prepared in advance. The absorbance of a blank solution was measured by AAS and its concentration was recorded. The absorbance readings and concentrations in each solution were carried out 10 times. The value of reading the blank solution was recorded and calculated to get the IDL value. The instrument detection limit (IDL) can be determined by the following formula:

$$\text{LOD} = \mu + 3\text{SD} \quad (4)$$

Where μ is the average value produced by measuring blanks with same reagent and SD is standard deviation value.

Furthermore, the spike solution for the MDL test which had been prepared before, measured the absorbance with AAS, the reading of each solution was done 10 times. The values on the results of reading the spike solution were recorded and calculated to get the MDL value. The MDL value can be determined by the following formula [10]:

$$\text{MDL} = t(0.01; n-1) \times \text{SD} \quad (5)$$

Where $t(0.01; n-1)$ is value obtained from table t with the level of freedom $n-1$ and a probability of 99% and SD is standard deviation.

3. Result and discussion

3.1. Solvent optimization

The first stage carried out in this research was optimum determination of solvent. Optimization of solvents aims to find out in solvents where lubricating oil can be completely dissolved. The determination of this solvent optimization uses three different types of organic solvents including n-hexane, thinner and methyl isobutyl ketone (MIBK). The direct dilution method with dissolution above was carried out on lubricant oil samples where the concentration was made varied were 0.5 ppm and 1 ppm. The absorbance of each solution was measured by AAS. The results of the best absorbance values from the two variations of the concentration were used as solvents in the direct dilution method in this research. The result measurement can be seen in figure 1.

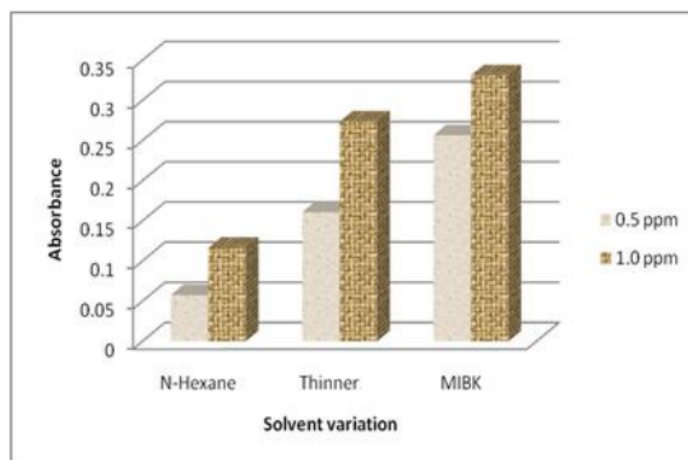


Figure 1. The optimization of solvent variation

Based on figure 1, it can be seen that the organic solvents having the best absorbance are in the solvent methyl isobutyl ketone (MIBK) for each concentration. These data indicate that MIBK solvents are the most stable in dissolving oil lubricants, thus providing the best absorbance response. MIBK solvents were then used in this research.

3.2. Linearity

The linearity test of Cd determination was carried out by measuring the absorbance of series standard Cd solutions at range concentration variation of 0.5 - 8.0 ppm, at a wavelength of 228.8 nm. Linearity test is expressed as a correlation coefficient (r), and the measurement results can be seen in figure 2.

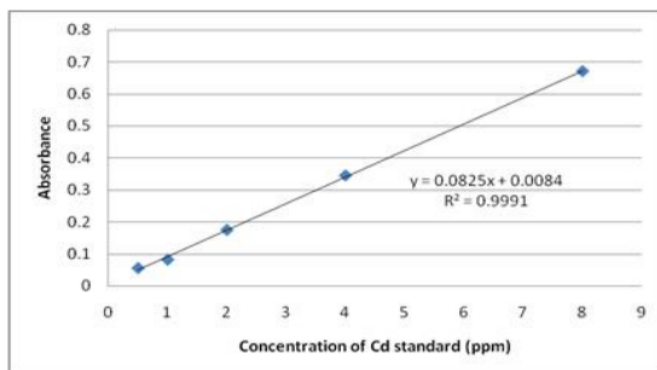


Figure 2. Calibration curve of Cd using AAS

The linear line equation obtained from the measurement results is $y = 0.0825x + 0.0084$, with the value of the coefficient of correlation (R^2) = 0.9991 and $r = 0.9995$. The value of $r = 0.9995$ indicates that the results of data linearity are declared valid and there is a very strong correlation between the concentration of standard solutions and absorbance [8, 9].

3.3. Accuracy

Accuracy is a value that shows the degree of similarity in the results of an analysis compared to the actual number of analytes. Accuracy can also be explained as percentage of recovery from an analyte for which standards are added standard and spiking method.

In this study the accuracy test was carried out by measuring lubricant oil samples which were then added to the standard. % Recovery was obtained by $91.65 \pm 0.017\%$. Accuracy results are stated to be good if the values obtained range from 80 - 110% [10]. The results of the accuracy test in this research are still in the specified range, so the data can be declared valid.

3.4. Precision

Precision is the degree of similarity between individual test results measured by the distribution of individual results based on the average if the procedure is performed repeatedly on samples obtained from homogeneous mixtures [10]. States that precision is measured as a standard deviation of the coefficient of variance (CV). Precision can be expressed as repeatability or reproducibility. At this stage, certain precision criteria which are included are standard deviation, % RSD and 2/3 CV Horwitz [11]. The measurement results can be seen in table 1.

Table 1. The result of measurement precision of oil lubricant samples with a dilution method

Analysis of Repeatability on day 1:	
% RSD \leq CV Horwitz	$0.0355 \leq 1.3806$
Analysis of Repeatability on day 2:	
% RSD \leq CV Horwitz	$0.0184 \leq 1.3920$
Repeatability	Accepted
Average	0,7280
Standard deviation	0.0358
% RSD	0.0492
Nilai Horwitz	2.0689
Reproducibility:	
% RSD \leq CV Horwitz	$0.0492 \leq 2.0689$
Reproducibility	Accepted

Based on the results of statistical calculations, the results obtained show that all the precision test results in this research both the repeatability and reproducibility parameters give, the % RSD $\leq 2/3$ CV Horwitz value, so it can be concluded that the data obtained has good precision values and data can be declared valid.

3.5. LOD and LOQ

LOD and LOQ are the lowest concentration of analyte and the smallest quantity that can be determined by a method that is fully applied to the method used with the conditions validated in the testing laboratory [12]. At this step, the limit detection test (LOD) and quantization limit (LOQ) were carried out statistically using the standard Cd calibration of curve obtained in the previous linearity test [10].

The measurement data shows that the LOD value of the determination of Cd using the AAS detector is 0.2209 ppm and LOQ is 0.7365 ppm. This value indicates that the amount of analytes that can still be measured by AAS. It can be concluded that for each measurement with the amount of analytes below the value of LOD and LOQ it can be declared undetected (not valid).

3.6. Instrument Detection Limit (IDL)

IDL parameters are different from LOD, LOQ and MDL. IDL is the lowest concentration of analyte that can be detected by the instrument and is statistically different from the response obtained with the response from the background signal.

The standard deviation obtained from the measurement of the amount of measured analytes from a blank sample of 10 times is 0.0207. The IDL value is obtained by formula 3 times the number of the standard deviation of blank [13] and the IDL value is 0.0622. This IDL value can be used for the smallest detection limit of the instrument used in this study. The AAS instrument used is still able to read analytes until the concentration is ± 0.0622 ppm.

3.7. Method of Detection Limit (MDL)

Determination of MDL (Method Detection Limit) is carried out to determine the limitations and ability of a laboratory in applying certain methods of testing at low analyte levels. Calculation of total sample volume, standard volume piped, standard concentrations pipetted and target concentrations obtained through calculations based on the results obtained in the previous IDL test. The MDL spike solution obtained was measured by its absorbance using AAS for 10 measurements. The making MDL spike solution (sample + standard) can be seen in table 2.

Table 2. Calculation of making spike solution.

Treatment	Calculation
Total sample volume	49 mL
Standard volume piped	1 mL
Standard concentration piped	9 ppm
Target concentration	0.18 ppm

MDL value obtained from value of $t(0.01; n-1) \times SD$. Based on the research that has been done, the standard deviation value is 0.011. Based on table t with a confidence level of 99%, if $n = 1$ is obtained number 2.821 [9]. MDL value obtained is 0.0346 ppm

The condition for accepting the MDL value if $MDL < [spike]$, indicates $0.0364 < 0.18$. Therefore, from the data obtained it can be concluded that the results of testing the MDL value have terms of acceptance and can be declared valid.

4. Conclusion

The direct dilution analysis method for determination of Cd metal in lubricating oil using AAS shows that all data obtained meets the acceptability requirements. The test results are declared valid, and can be used for routine analysis.

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