Analysis of Uncertainty in the Detection of Ca, Zn, and P Elements in Lubricants Using the ICP-OES Methodology

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Abstract. This article presents a study that evaluated the uncertainty in determining additive elements in lubricating oils. The aim of the study was to develop an uncertainty assessment process for calcium, phosphorus, and zinc, identifying the main sources of uncertainty and proposing improvements in the analysis process. The study utilized the technique of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) to perform the measurements of the additive elements. Three analysts were selected to conduct the measurements in the same system, and the conditions of repeatability were evaluated for each analyst. Several sources of uncertainty were identified, including the analytical standard, calibration curve, volumetric dilution, glassware calibration and resolution, balance resolution and calibration, as well as repeatability. The results showed that analysts Y and Z obtained results within the specified limits, indicating good trueness and precision. On the other hand, analyst X yielded results close to the lower limits, highlighting the importance of analyst training and experience. One of the main conclusions of the study was the need for optimization in the sample preparation process, suggesting the substitution of volumetric dilution with mass dilution as a viable option to reduce sources of uncertainty and improve result reliability. In summary, the study emphasizes the importance of uncertainty assessment in determining additive elements in lubricating oils, emphasizing the need to understand and quantify sources of uncertainty to make reliable decisions and strive for more accurate results. Additionally, it highlights the significance of adequate analyst training and the implementation of rigorous sample preparation procedures to achieve reliable and high-quality results.

1. Introduction

As per the ASTM (American Society for Testing and Materials) D4175 standard [1], which aims to standardize terminologies related to Petroleum Products, Liquid Fuels, and Lubricants, Lubricating Oils are defined as "a liquid lubricant, usually comprising several ingredients, including a major portion of base oil and minor portions of various additives." The additives present in oils offer advantages in terms of performance, as they can confer, enhance, or suppress properties in order to achieve specific desired results or eliminate undesirable characteristics. Given these facts, the importance of the additive process is evident, as well as the need for a solid methodological framework for the quantitative determination of these elements.

In this context, the ASTM D4951 standard [2] stands out, aiming to standardize the determination of additive elements in used lubricating oils by Inductively Coupled Plasma Atomic Emission

Spectroscopy (ICP-AES) or also known as Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Among the various methods available for elemental quantification, ICP-OES stands out for its high sensitivity and ability to measure multiple elements simultaneously. In the case of the ASTM D4951 standard, nine elements are specifically considered: barium, boron, calcium, copper, magnesium, molybdenum, phosphorus, sulfur, and zinc, with the precision of this assay determined by statistical analysis of inter-laboratory results.

However, the quantitative determination of additive elements in lubricating oils requires the application of analytical techniques that can introduce uncertainties in the obtained results. Faced with this need, the Quality Control Laboratory of the VIBRA ENERGIA Lubricants factory undertook an uncertainty evaluation study with the intention of quantifying the expected variation in measurement results and providing an estimate of the reliability of the obtained results. This approach seeks to demonstrate the transparency and accuracy of the measurement process, which is particularly relevant in industrial contexts where decision-making and product quality assurance depend entirely on the data obtained.

Therefore, the objective of this study was to develop a process for evaluating the uncertainty in the quantitative determination of the additive elements calcium, phosphorus, and zinc in lubricating oils. The main purpose was to identify the most relevant sources of uncertainty in order to propose effective improvements that could be implemented in an enhanced manner. The primary goal was to identify and understand the abilities and competencies of the analysts involved in the analysis process. This included identifying possible knowledge gaps or the need for additional training for the analysts, encompassing aspects such as academic background, practical experience, training in analytical techniques, the ability to interpret results, and make appropriate decisions. By doing so, the study aimed to enhance the overall accuracy and reliability of the measurement process.

2. Materials and Methods

2.1. Experimental setup

The concentration determination of metals was performed using the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) instrument, specifically the PerkinElmer's Avio 500 model, as shown in Figure 1. ICP-OES is an analytical technique that utilizes a high-temperature argon plasma to ionize and excite the elements present in a liquid sample. The electromagnetic radiation emitted by the excited elements is detected by a spectrometer, enabling the identification and quantification of the elements present.
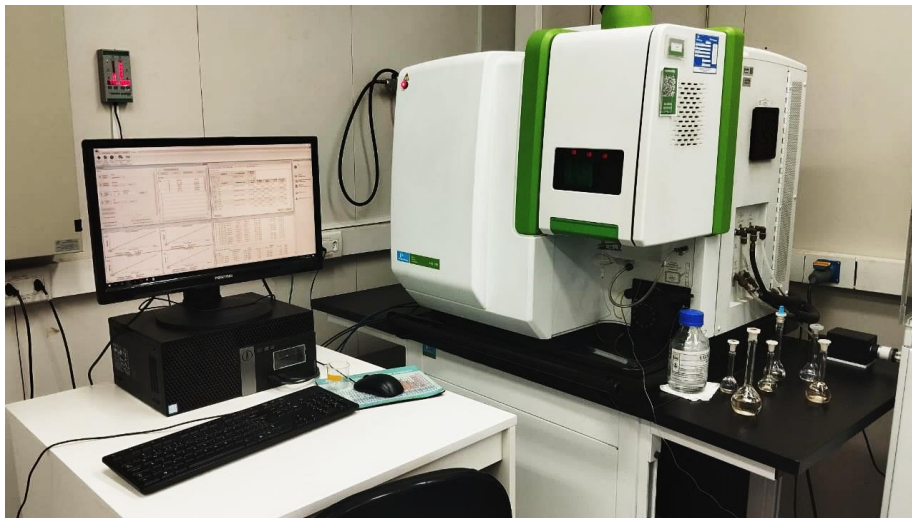
Figure 1. Experimental setup using ICP-OES, PerkinElmer's Avio 500 model.

The mass measurement of the samples was performed using the analytical balance model Sartorius MSU225P-1CE-DU, with a precision of 0.1 mg. For sample and standard preparation, volumes were determined using 50 mL volumetric flasks, ensuring appropriate dilution. Additionally, the temperature and humidity of the environment where the measurements were carried out were continuously monitored using the termo-hygrometer model Minipa MT-242ª. All instruments used underwent proper calibration to ensure the reliability of the obtained results.

Table 1. Instrumental parameters used in measurements on the Avio 500 ICP-OES.

Parameter	Value
Nebulizer	Borosilicate Glass MEINHARD Type K1 Concentric Nebulizer
Spray Chamber	Baffled glass cyclonic
RF Power	1500 W
Torch	3-slot Avio torch for organics
Read Delay	16 sec
Torch Position	-3
Replicates	6
Integration Range	0.5 - 2.0 sec

2.2. Preparation of the Analytical Curve

The preparation of the Analytical Curve was carried out using seven concentration ranges: 0.0 mg/L, 2.5 mg/L, 5.0 mg/L, 10.0 mg/L, 20.0 mg/L, 40.0 mg/L, and 60.0 mg/L. To obtain a linear Analytical Curve, the method of least squares (MLS) was used, with six replicate readings of intensities for each of the seven standard concentrations. A commercial standard from the brand CONOSTAN® Additive Metal Special was used. This multi-element standard contains barium (Ba), calcium (Ca), magnesium (Mg), phosphorus (P), and zinc (Zn), specifically designed for the lubricant industry. The standard had a concentration of 2000 ppm (Wt.).

2.3. Measurement Procedure

For this study, three technicians were selected, and six repetitions were performed under repeatability conditions by each technician. As stated in Table 1, each of the six measurements corresponds to the average of another six repetitions, which were previously defined as inherent parameters of the equipment in question. All technicians received the same sample; however, no information about the sample content was provided to avoid any bias in the data. In this case, a sample of the product Top Turbo, considered the main product for diesel engines in the SAE 15W-40 grade, was selected for analysis.

It is important to highlight that each technician performed the calibration of their analytical curves before starting the measurement process. This calibration was done using the same previously prepared solutions, ensuring that there was no propagation of errors related to the preparation procedures of standard concentrations. In this way, efforts were made to minimize any external influences that could affect the trueness and precision of the measurements directly linked to the samples.

2.4. Expression of Uncertainty

In the uncertainty evaluation process, understanding the mathematical model involved in the system is essential as it allows for a precise description of the relationships between the different variables in the measurement process. By establishing a mathematical model, it becomes possible to represent the relationships between these variables clearly, facilitating the identification of the main

sources of uncertainty and their impact on the final results. The mathematical model of this study can be observed in equation 1 [3], below:
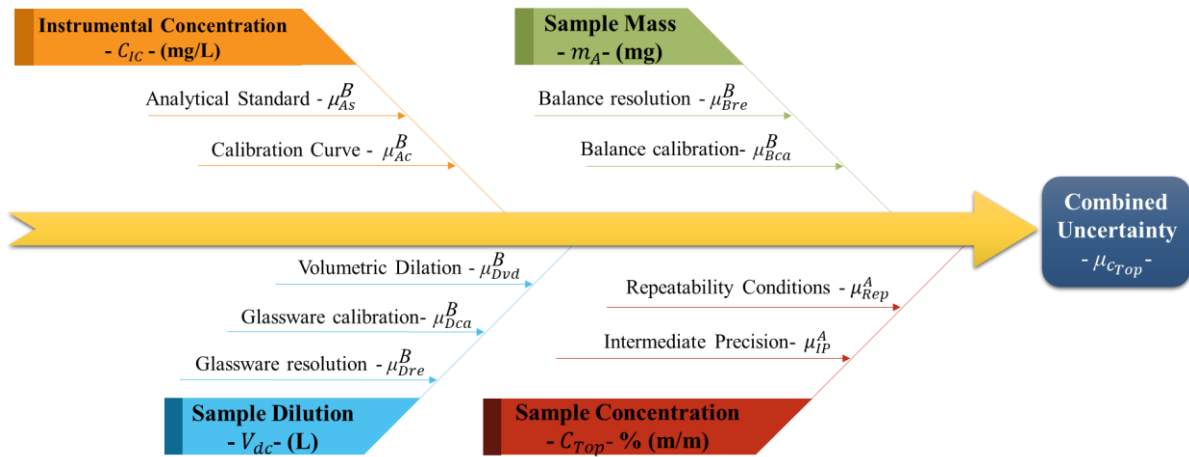
$$C_{Top} = \frac{C_{IC} * V_{dc}}{m_A * 10000}$$ (1)

Where:
C_{Top} = Sample Concentration (mg/kg)
C_{IC} = Instrumental Concentration (mg/L)
V_{dc} = Volume of Sample Dilution (L)
m_A = Mass of Weighed Sample (kg)

Figure 2. Ishikawa diagram for random effects in the determination of Ca, Zn, and P in Top Turbo Lubricant samples.

Through the diagram (Figure 2), we can group the sources of uncertainties into four categories: Instrumental Concentration, Sample Dilution, Sample Mass, and Sample Concentration.

2.4.1. Concentration. In Instrumental Concentration, uncertainties of type B are incorporated, including those from the calibration certificate of the standard (μ_{As}^B) and the Calibration of the Analytical Curve (μ_{Ac}^B), which is obtained through equations 2 and 3 [4].

$$\mu_{Ac}^B = \frac{S_r}{b} \sqrt{\left(\frac{1}{p} + \frac{1}{n} + \frac{(C_{IC} - \bar{C})}{\sum_1^n(C_i - \bar{C})}\right)}$$ (2)

S_r is calculated by equation 3:

$$S_r = \sqrt{\frac{\sum_{j=1}^n(I_i - (a + bC_i))^2}{n - 2}}$$ (3)

Where:

μ_{Ac}^{B} = Uncertainty in the Calibration of the Analytical Curve (mg/L);

S_r = Residual Standard Deviation (mg/L);

C_{IC} = Sample Concentration (mg/L);

$\bar{C}$ = Overall Mean of Standard Concentrations (mg/L);

C_i = Concentration of Standard i (mg/L);

p = Number of measurements to determine C_{IC};

n = Number of measurements to perform the calibration;;

I_i = Signal intensity in the jth reading;

b = Slope;

a = Intercept.

2.4.2. Sample Dilution. The uncertainties of type B are incorporated, including those from the resolution of glassware (μ_{Dre}^{B}), the calibration certificate of the glassware (μ_{Dca}^{B}), and the Volumetric Dilution (μ_{Dvd}^{B}), given by Equation 4.

$$\mu_{Dvd}^{B} = \frac{VK \, \Delta t}{\sqrt{3}} \tag{4}$$

Where:

V = Sample Volume (L);

K = Coefficient of volumetric expansion of EXXSOL, the solvent used in sample dilution (with a value of 7.4×10^{-4} °C^{-1});

Δt = Thermal variation range (The average laboratory temperature during the measurements was 21.18 ± 1.30 degrees Celsius).

2.4.3. Sample Mass. The uncertainties of type B are incorporated, including those from the resolution of the balance (μ_{Bre}^{B}) and the calibration of the balance (μ_{Bca}^{B}). The eccentricity was not incorporated as its value in the calibration certificate is null.

2.4.4. Sample Concentration. When we have an estimate of an input quantity based on n measurements performed under repeatability conditions (μ_{Rep}^{A}), the type A uncertainty can be determined by calculating the standard deviation of the mean, as expressed in equation 5 [5].

$$\mu_{Rep}^{A} = \frac{S_{Rep}}{\sqrt{n_{Rep}}} \tag{5}$$

Where:

S_{Rep} = Standard Deviation for repeatability (mg/L);

n_{Rep} = Total number of measurements;

2.4.5. Combined and Expanded Uncertainty. The combined uncertainty of the concentration of Top Turbo samples ($\mu_{c_{Top}}$) was obtained using equations 6, in which it is possible to identify the sensitivity coefficients (C_x^S) associated with each source of uncertainty, and in Table 2, their respective values are presented.

$$\mu_{c_{Top}} = \sqrt{\begin{array}{c}((\mu_{As}^B.C_{As}^S)^2 + (\mu_{Ac}^B.C_{Ac}^S)^2) + ((\mu_{Dvd}^B.C_{Dvd}^S)^2 + (\mu_{Dca}^B.C_{Dca}^S)^2 + (\mu_{Dre}^B.C_{Dre}^S)^2) \\ + ((\mu_{Bre}^B.C_{Bre}^S)^2 + (\mu_{Bca}^B.C_{Bca}^S)^2) + (\mu_{Rep}^A)^2\end{array}} \qquad (6)$$

Table 2. Sources of uncertainty and their respective sensitivity coefficients.

Component of Uncertainty		Sensitivity Coefficient (C_x^S)
Instrumental Concentration	μ_{As}^B - Analytical Standard	$-\dfrac{C_{Pa*}V_{dc}}{m^2 * 10000}$
	μ_{Ac}^B - Calibration Curve	
Sample Dilution	μ_{Dvd}^B - Volumetric Dilation	$\dfrac{C_{Pa}}{m * 10000}$
	μ_{Dca}^B - Glassware calibration	
	μ_{Dre}^B - Glassware resolution	
Sample Mass	μ_{Bre}^B - Balance resolution	$\dfrac{V_{dc}}{m * 10000}$
	μ_{Bca}^B - Balance calibration	
Sample Concentration	μ_{Rep}^A – Repeatability	1

Based on the results of the combined uncertainty, it was possible to calculate the expanded uncertainty using equation (7). The expanded uncertainty is expressed as a confidence interval, defined by the coverage factor (k) multiplied by the combined uncertainty. The value of k is determined based on the desired confidence level, in this case, a confidence interval of 95% was used [5].

$$U_{exp} = k*\mu_{c_{Top}} \qquad (7)$$

3. Results and Discussion

The analysis of the results obtained for the concentration of the additive elements calcium, phosphorus, and zinc was conducted, considering the repeatability conditions for each analyst, as presented in table 3. Three analysts, named X, Y, and Z, were selected to perform the measurements in the same measurement system.

Table 3. Average values of each Analyst, with their respective uncertainties expanded in repeatability condition for each element.

	Ca		P		Zn	
Analysts	Mean Concentration (mass %)	U_{exp} (mass %)	Mean Concentration (mass %)	U_{exp} (mass %)	Mean Concentration (mass %)	U_{exp} (mass %)
X	0.3300	0.0101	0.0930	0.0065	0.0982	0.0062
Y	0.3697	0.0032	0.1007	0.0024	0.1054	0.0022
Z	0.3649	0.0024	0.0976	0.0016	0.1026	0.0014

The data presented in Table 3 the result of a careful and detailed mapping of various sources of uncertainty associated with the measurements of the elements. Understanding and quantifying these uncertainties are essential to support informed decisions, improve result reliability, and allow for a more accurate assessment of the quality of the obtained data. In Figure 3, it is possible to visualize the specific contributions of each source of uncertainty considered in this study, which facilitates the understanding of the individual performance of each analyst.
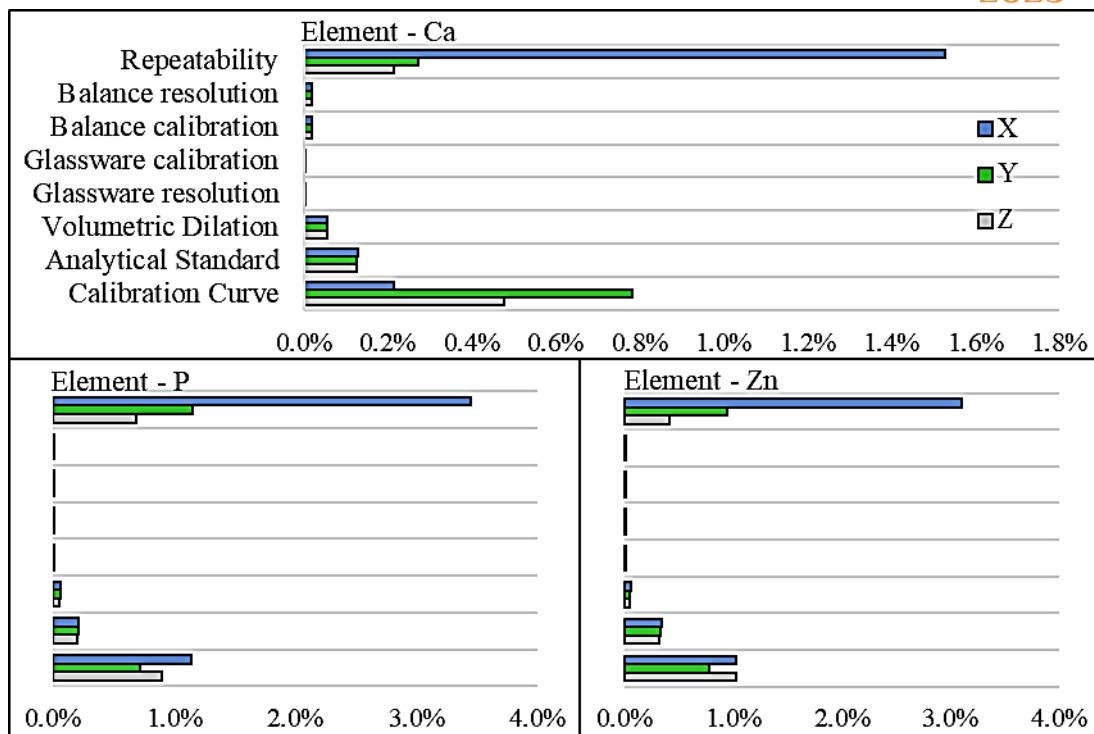
Figure 3. Contribution of uncertainty sources from the average in the determination of Ca, P and Zn for three analysts X, Y and Z.

When analyzing Figure 3 and Table 3, it becomes evident that there are discrepancies in the uncertainty values associated with Analyst X compared to the other analysts. Through the proper identification of sources of uncertainty, it is possible to observe that this discrepancy is directly related to repeatability values. Based on the methodology used in this study, it can be inferred that Analyst X may require additional training in sample preparation to minimize variability in measurements.

Furthermore, it is interesting to note that, for all analysts and elements evaluated, the main sources of uncertainty associated with the ICP-OES methodology in lubricant analysis are the preparation of the standard used for calibration of the analytical curve and the preparation and analysis of samples related to repeatability results. These process steps have a significant impact on the total uncertainties of the measurements. Therefore, it is crucial to adopt appropriate measures to control and reduce uncertainties related to these sources in order to ensure more accurate and reliable results in the determination of additive elements in lubricating oils.

To assess the agreement between analysts' results within a single measurement system, we conducted an intermediate precision study based on the previously presented data. We compared the concentrations of additive elements obtained by different analysts on different days using the same equipment. However, following the guidelines established by DOQ-CGRE-008, it is advisable to perform a preliminary analysis to determine whether the tested groups can be considered statistically similar. Therefore, we proceeded with an analysis of variance (ANOVA), the results of which are presented in Table 4. [6]

Table 4. ANOVA of Analysts X, Y, and Z.

Source of Variation	Ca	P	Zn
Mean	0.3549	0.0971	0.1021
F	52.27	3.74	3.80
p-value	1.73E-07	0.05	0.05
Critical F	3.68	3.68	3.68

Based on the results presented in Table 4, it can be observed that for all elements, the p-value is equal to or less than 0.05, and the F-values exceed the critical limit. This set of evidence leads us to reject the null hypothesis that the effects of the analysts are negligible, clearly indicating a direct interference of analysts in the results.

However, upon examining the data presented in Table 3 and Figure 3, it is evident that there is a more pronounced deviation in the concentrations associated with Analyst X. In order to emphasize this discrepancy, we conducted a Tukey test, and Table 5 unequivocally demonstrates that Analysts Y and Z do not show statistically significant differences in relation to any of the elements, unlike Analyst X.

Table 5. Tukey's Test at 5%.

	Ca	P	Zn
Y	a	a	a
Z	a	a/b	a/b
X	b	b	b

Equal letters indicate that, at the 5% significance level, there is no difference between the means.

Based on this investigation, it becomes evident that the available data are insufficient to conduct an intermediate precision study robustly. The main limitation lies in the fact that only the data collected between technicians Y and Z do not provide a solid enough foundation to support a reliable analysis. Therefore, it is crucial to consider the incorporation of additional datasets to strengthen the study's foundation and achieve more meaningful results.

3.1. Control Limits

As described in ASTM D4951 standard, it is necessary for every product to have its average value and upper and lower limits specified to monitor its measurement process. In Table 6, we can observe the specifications of the Top Turbo product along with the estimated repeatability by ASTM itself. Figure 4 displays the repeatability results of the analysts (Table 3) compared to the specification parameters for each element present in the Top Turbo lubricant. This comparison is crucial to verify if the results obtained by the analysts are within acceptable limits and meet the established quality requirements.

Table 6. Control Specifications for Top Turbo.

	Ca		P		Zn	
	Concentration (mass %)	ASTM Repe.	Concentration (mass %)	ASTM Repe.	Concentration (mass %)	ASTM Repe.
Lower Limits	0.3290	±0.0089	0.0890	±0.0023	0.0980	±0.0022
Upper Limits	0.3960	±0.0097	0.1100	±0.0029	0.1200	±0.0026
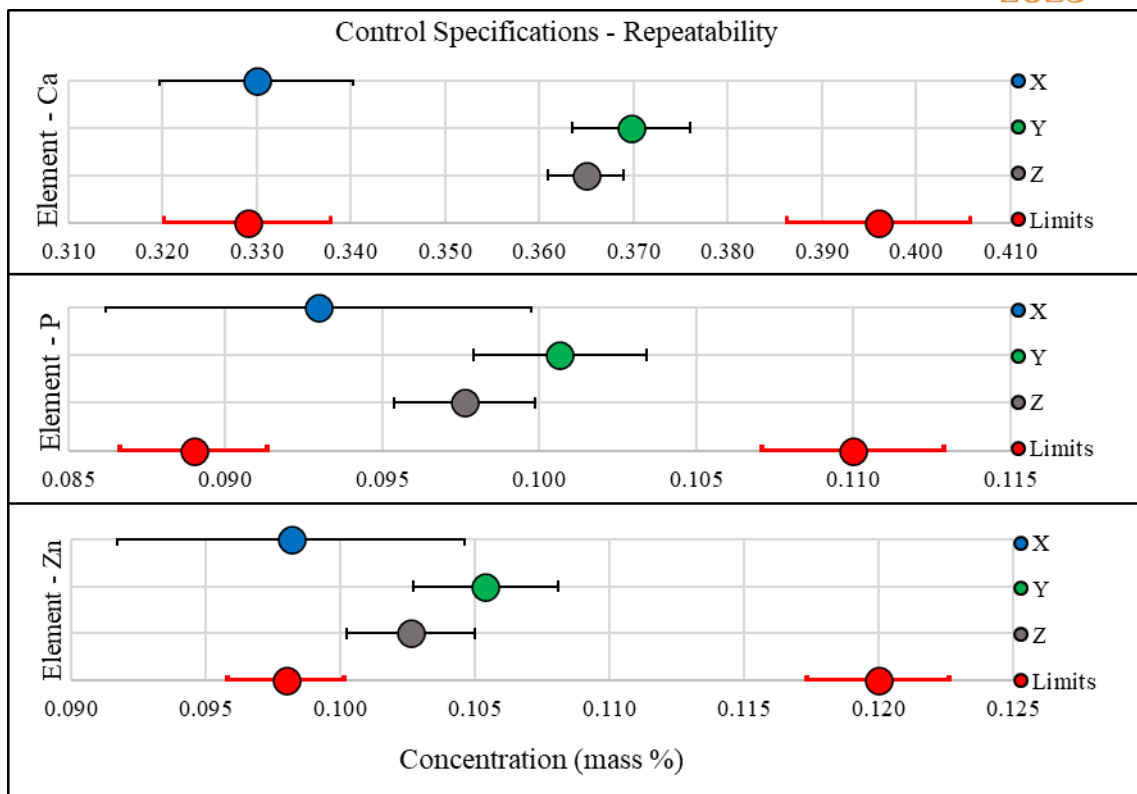
Figure 4. Relationship between Uncertainty Values of Analysts under Repeatability Conditions and Specifications of Top Turbo Product for Ca, P, and Zn Elements.

Through Figure 4, the discrepancy in the results obtained by Analyst X becomes evident, both in terms of trueness and precision, with borderline results, close to the lower limits. This result from Analyst X was expected, as among the three selected analysts, they were the only one who had not completed their full training and were not part of the technical team responsible for ICP-OES analyses. This methodology was intentionally introduced to demonstrate practically the effectiveness of a process in mapping related sources of uncertainty and revealing where optimization is needed.

It is also interesting to note that based on the data obtained, Analysts Y and Z maintained their results within a relatively safe margin, being within the specification limits in all cases. However, considering the methodological observations employed, several optimization options have been identified that can lead to even better results. One of these factors is replacing volumetric dilution with mass dilution. This is justified by the fact that small variations in volume measurement can result in significant variations in the final concentration, especially when the initial concentrations are low, as is the case in this study. These variations can compromise the accuracy of the results and introduce significant uncertainties in the quantitative determination of elements. Additionally, volumetric dilution is susceptible to external influences such as temperature and pressure, which can affect the actual volume added. These variations in environmental conditions can contribute to result uncertainty. Therefore, considering the context of uncertainty, replacing volumetric dilution with mass dilution may be a viable alternative to reduce these sources of uncertainty and increase the reliability of analytical results.

4. Conclusions

Based on the conducted study, the importance of a solid methodological framework for the quantitative determination of additive elements in lubricating oils becomes evident. The ASTM D4951 standard plays a fundamental role in this context, standardizing the analysis procedures through the ICP-

OES technique. Several sources of uncertainty associated with the measurements of calcium, phosphorus, and zinc additive elements were identified during the study. Understanding and quantifying these uncertainties are essential to ensure result reliability and support informed decisions. The results obtained by Analysts Y and Z demonstrated good precision and accuracy, being within the specified limits for the Top Turbo product. However, Analyst X presented borderline results, close to the lower limits, which was expected due to the lack of complete training and experience in ICP-OES analysis.

Among the identified sources of uncertainty, volumetric dilution used in the sample preparation process stood out as a factor that can introduce significant errors. Small variations in volume measurement can result in significant variations in the final concentration, especially when the initial concentrations are low. Additionally, external factors such as temperature and pressure can affect the actual volume added, contributing to result uncertainty. Therefore, considering the context of uncertainty, replacing volumetric dilution with mass dilution emerges as a viable option to reduce sources of uncertainty and improve the reliability of analytical results. This optimization can be achieved through proper training of analysts and implementation of rigorous sample preparation procedures.

The conducted study highlights the importance of uncertainty evaluation in the analysis processes of additive elements in lubricating oils. This approach allows identifying the most relevant sources of uncertainty and proposing effective improvements, ensuring transparency and accuracy in the measurement process. Through this process, knowledge gaps and the need for additional training of analysts can be identified, contributing to the continuous improvement of result quality. In conclusion, the study emphasizes the importance of a solid methodological framework, uncertainty assessments, and the pursuit of optimizations in the determination process of additive elements in lubricating oils. These practices are essential to ensure result reliability, meet quality requirements, and make informed decisions based on the obtained data.

References

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