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Rapid Monitoring of Key Alloying Elements in Deformed Steel Bars Using Portable EDXRF and LIBS: A Strategy Against Substandard Quality

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***Abstract* - This study investigates the effectiveness of combining portable analytical techniques - Energy Dispersive X-ray Fluorescence (EDXRF) and Laser-Induced Breakdown Spectroscopy (LIBS) - as alternatives to traditional Spark Optical Emission Spectroscopy (Spark-OES) for the rapid assessment of key alloying elements Carbon (C), Silicon (Si), Manganese (Mn), Phosphorous (P) and Sulfur (S) in deformed steel bars.**

Both EDXRF and LIBS demonstrated strong accuracy and precision in analyzing C, Si, and Mn, with statistical analysis revealing significant correlations with the Spark-OES benchmark. However, detection of P and S requires further optimization due to inherent analytical challenges. The combination of these portable methods offers substantial advantages, including on-site testing capabilities and minimal sample preparation, enabling real-time monitoring and immediate quality control.

The findings underscore the potential of EDXRF and LIBS to enhance quality assurance processes in the steel industry, promoting safer construction practices through efficient, non-destructive testing methods.

Keywords: LIBS, EDXRF, Spark-OES, deformed steel bars, quality assurance

I. INTRODUCTION

The increasing global demand for steel products has intensified the focus on the integrity and quality of reinforcing materials, particularly deformed steel bars that are critical for construction. According to the World Steel Association, global crude steel production reached 1,950.5 million metric tons in 2022, reflecting a 3.1% increase from the previous year [1]. This growth, largely driven by infrastructure development and industrialization across emerging economies in Asia, Africa, and Latin America, has been accompanied by concerns regarding the prevalence of substandard rebar—steel bars that fail to meet established quality standards. Substandard materials often exhibit deficiencies in chemical composition and mechanical properties, increasing the risk of catastrophic structural failures, property damage, injuries, and loss of life [2].

International standards such as ASTM A615, BS 4449, ISO 6935-2, and PNS 49:2020 set testing protocols and permissible limits for critical alloying elements, including C, Mn, Si, P, and S, to ensure the mechanical integrity and safety of reinforcing steel [3], [4].

Key alloying elements play vital roles in the performance of deformed steel bars. C increases hardness and tensile strength but can reduce ductility. Si acts as a deoxidizer, improving strength, ductility, and corrosion resistance. Mn enhances toughness, hardness, and mitigates sulfur-induced brittleness. P can boost strength and machinability but must be controlled to avoid embrittlement. S improves machinability but may cause brittleness if excessive. Careful balancing of these elements is essential to achieve the desired mechanical properties for construction use [3].

The use of inferior steel undermines public trust, prompts stricter regulations, and increases environmental impacts due to waste and carbon emissions [5]. Advanced on-site verification technologies are thus critical. While Spark-OES provides accurate elemental analysis, it requires destructive testing, extensive preparation, and long turnaround times [6].

In contrast, portable EDXRF and LIBS devices offer rapid, non-destructive analysis with minimal preparation, enabling real-time quality control at construction sites [7]. These handheld tools are fast, cost-effective, and user-friendly [8], enhancing compliance monitoring and construction safety. However, studies on their use for reinforcing steel bar analysis remain limited [9]. This study addresses that gap by comparing handheld LIBS and EDXRF analyzers with laboratory-based Spark-OES for quantifying C, Si, Mn, P, and S in deformed steel bars [10], [11].

The assessment evaluates analytical accuracy, repeatability, precision, and operational efficiency under field conditions. Statistical tools such as Pearson's correlation, linear regression, and relative standard deviation were used to validate performance. The goal is to establish a reliable, rapid, non-destructive method for on-site quality control of reinforcing steel, promoting safer and more sustainable infrastructure.

II. METHODOLOGY

This study evaluates the accuracy of handheld instruments—EDXRF and LIBS—as alternatives to Spark Spark-OES for the rapid analysis of key alloying elements (C, Si, Mn, P, and S) in deformed steel bars. EDXRF was used to assess Mn, Si, P, and S, while LIBS was applied for C, Si, and Mn. Validation employed certified reference materials (CRMs/SRMs), with comparative analyses conducted against Spark-OES as the benchmark. Statistical methods, including Pearson's correlation coefficient and linear regression, were used to determine the analytical performance of the portable devices.

A. Instrumentation and measurement conditions

The SCIAPS X-200 handheld EDXRF was employed for non-destructive multi-element analysis, operating with a rhodium (Rh) anode X-ray tube at 30–50 kV and a silicon drift detector (SDD) achieving 130 eV energy resolution at 5.9 keV. EDXRF identifies elements based on secondary X-ray emissions with minimal sample preparation. The SCIAPS Z-200 C+ handheld LIBS device was used for in-situ analysis, generating a plasma plume via a high-energy laser pulse, allowing rapid (~15 seconds) detection of elements from carbon to uranium. Spark-OES analysis was performed with the SPECTROMAXX LMF07, utilizing an electric arc or spark to vaporize the sample and detect elemental emissions with high precision but requiring extensive sample preparation.

For EDXRF, exposure times ranged from seconds to minutes, covering a spectral range of 3–40 keV. LIBS exposure times varied from microseconds to milliseconds across a spectral range of 190–625 nm. Spark-OES operated within 180–800 nm, with exposure times of milliseconds to seconds optimized to prevent detector saturation.

B. Analytical Signals and Calibration

Analytical signals were based on emission intensities: secondary X-rays for EDXRF, plasma emissions for LIBS, and atomic emissions for Spark-OES. Calibration for all methods utilized Certified Reference Materials CRMs/ /Standard Reference Materials (SRMs). EDXRF and LIBS applied multi-point calibration curves to correlate signal intensity with elemental concentrations, while Spark-OES calibration involved multi-element standards and internal standards to correct for plasma variations. Regular validation against CRMs ensured measurement consistency across methods.

C. Sample preparation

Nine (9) deformed steel bar samples with diameters of 10–50 mm were prepared (Figure 1). Samples were cut into ~25 mm lengths and ground with P60-grit aluminum oxide sanding paper. The 10 mm rebars were flattened longitudinally to create a sufficient test surface. Ten measurements per sample and CRM were collected. CRMs from Bureau of Analyzed Spls., Ltd., Brammer Standards Co., Inc., and MBH Analytical Ltd., traceable to NIST, were used, targeting concentration ranges specified in PNS 49:2020.

Fig. 1 *Nine (9) deformed steel bar samples (top) were collected from different local manufacturers and certified reference materials (bottom) used in this study.*

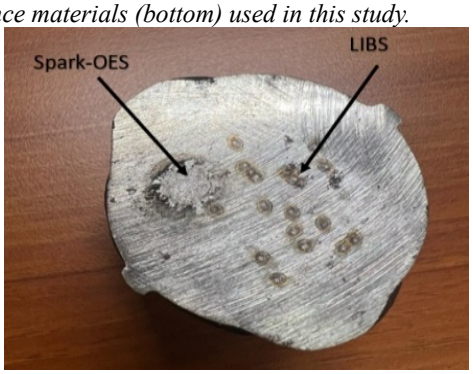

Fig. 2 *The localized shots on the sample surface where the material was ablated by the spark in OES or the laser in LIBS.*

Figure 2 illustrates the localized ablation differences between Spark-OES and LIBS, Spark-OES generated larger ablation areas (~1 mm diameter; 10–100 µm depth), while LIBS produced finer shallower ablations (50–500 µm diameter; 1–10 µm depth).

D. Chemometric statistical analysis

Validation of the methods was conducted using CRMs/SRMs to assess both accuracy and precision. The accuracy was evaluated through percentage recovery (% Recovery) and the precision was assessed using the percentage relative standard deviation (% RSD). Recovery rates obtained from each method were compared against established thresholds from AOAC peer-verified methods [12].

This systematic approach ensured that the methods employed were reliable and capable of providing accurate elemental analyses of the samples. On the other hand, the data gathered from the analysis of rebar were statistically treated using Pearson's correlation coefficient and linear regression coefficient of determination.

III. RESULTS AND DISCUSSIONS

A. Instrument verification

The suitability of the three methods in the chemical analysis of rebar was verified using CRM/SRM described in Section 2.2. Moreover, due to technical limitations of the handheld instruments, EDXRF was limited to detecting Si, Mn, P, and S, while LIBS could only analyze C, Si, and Mn. The results are presented in **Table 1**.

Following the limits for % recovery and % RSD stated in the AOAC peer-verified methods program (AOAC 1998) [12] which are 90 – 107 % recovery and 5.3 % RSD for an analyte concentration of 0.01%, 95 – 105 % recovery and 3.7 % RSD for an analyte concentration of 0.1%, and 97 – 103 % recovery and 2.7 % RSD for an analyte concentration of 1%, Based on the comprehensive assessment presented in the data, we can evaluate the performance of both the LIBS and EDXRF methods compared to the established Spark-OES benchmark.

The LIBS technique demonstrated impressive accuracy and precision across key alloying elements. For C, recovery ranged from 100.06% to 106.62%, well within the AOAC standards for a 0.1% analyte concentration, with excellent precision (RSD 0.68–2.93%). Si showed similarly outstanding results, with recovery between 99.30% and 101.77% and RSD values between 0.04% and 1.65%, fully complying with AOAC criteria. Mn also exhibited high performance, achieving recoveries from 97.00% to 101.94% and precision levels of 0.31–2.13%. The LIBS method consistently matched or exceeded the accuracy and precision benchmarks set by Spark-OES.

Turning to the EDXRF technique, the results were notable, though with some variation , For Si, recovery ranged

Table 1 *Quality Statistical Assessment for EDXRF and LIBS against Spark-OES*

			METHODS								
			EDXRF			LIBS			Spark-OES		
Analyte	CRM/ SRM	Ref. Value, %wt.	Mean, µ %w	% Recovery	% RSD	Mean, µ %wt. (n=10)	% Recovery	% RSD	Mean, µ %wt.	% Recovery	% RSD
Si	433/1	0.18	0.177	98.5	9.19	0.1787	99.3	1.65	0.180	100.32	0.8371
	401/1	0.41	0.405	98.88	2.46	0.4173	101.77	0.04	0.403	98.33	0.8545
	458/1	0.54	0.548	101.52	1.38	0.5409	100.16	0.31	0.540	100.06	0.8291
Mn	455/1	0.4	0.403	100.78	2.63	0.4012	100.3	1.88	0.400	100.15	0.3706
	454/1	0.8	0.786	98.3	2.15	0.803	100.38	0.98	0.802	100.28	0.2188
	BSHICAL	1.00	1.031	103.1	1.61	1.0194	101.94	2.13	1.006	100.69	0.6426
	434/1	1.49	1.552	104.18	0.9	1.4896	97	0.84	1.490	100.05	0.554
P	432/1	0.024	0.025	105.42	6.98	nd	ma	na	0.024	100.13	3.8205
	452/1	0.035	0.036	104	8.71	nd	na	na	0.035	100.46	1.2079
	434/1	0.055	0.051	93.74	3.77	nd	na	na	0.051	93.46	5.4042
S	401/1	0.009	0.010	117.78	2.63	nd	na	na	0.009	100.28	2.1582
	458/1	0.033	0.032	98.18	3.9	nd	na	na	0.033	100.8	0.6829
	455/1	0.055	0.052	95.45	5.1	nd	na	na	0.055	100.35	0.9184
C	12X12747	0.149	nd	na	Na	0.1589	106.62	2.93	0.148	99.8	0.4936
	452/1	0.318	nd	na	Na	0.3185	100.16	0.76	0.318	99.43	0.3703
	434/1	0.41	nd	na	Na	0.41	100.06	0.68	0.412	100.61	0.7118

na-not applicable; nd-not detected

from 98.50% to 101.52%, aligning well with Spark-OES results; however, precision was slightly lower, with RSD values from 1.38% to 9.19%, occasionally exceeding AOAC recommended limits. Mn analysis by EDXRF displayed excellent accuracy (98.30% to 104.18%) and acceptable precision (RSD 0.90–2.63%), meeting AOAC requirements. In contrast, for P, the EDXRF recovery was slightly outside the AOAC acceptable range at 105.42%, and the RSD value of 6.98% did not meet the 2.7% standard. Similarly, S showed a recovery of 117.78%, exceeding the AOAC limits, although precision remained reasonable.

Both LIBS and EDXRF demonstrate strong potential as viable alternatives or complementary techniques to Spark-OES for the rapid analysis of alloying elements in the steel industry. LIBS consistently meets or exceeds AOAC standards, while EDXRF performs well for major elements such as Si and Mn but may require optimization for trace elements like P and S.

B. Comparative analysis of rebar

The measurements of LIBS and EDXRF of rebar samples are presented in **Table 2**. Data were subjected to statistical relationship among the analytical methods. Pearson's analysis, and correlations were determined to examine the correlation coefficient expressed as r_{xy}, was calculated using Equation 1. x_i and y_i are the individual data points, $\bar{x}$ and $\bar{y}$ are the means of the respective data sets. The value ranges from -1 to 1. A correlation of 1 indicates a perfect positive linear relationship, -1 indicates a perfect negative linear

$$r_{xy} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2}\sqrt{\sum_{i=1}^{n}(y_i - \bar{y})^2}} \quad (1)$$

relationship, and 0 indicates no linear relationship. Data were also regressed to find the best fitting straight line that describes the linear relationship between the two analytical methods following Equation 2, where β_0 is the intercept, β_1 is the slope (coefficient), and ε represents the error term.

$$Y = \beta_0 + \beta_1 X + \varepsilon \quad (2)$$

$$R^2 = {r_{xy}}^2 \quad (3)$$

***Table 2**. Comparison of experimental values using OES, LIBS and, EDXRF with PNS 49*

Rebar sizes, METHOD	% C	% Si	% Mn	% P	% S
10mm, OES	0.3235	0.2339	0.8216	0.0168	0.0207
10mm, LIBS	0.3227	0.2341	0.8259	n.d.	n.d.
10mm, EDXRF	n.d.	0.2321	0.8249	0.0116	0.0215
16mm, OES	0.3201	0.2305	0.8018	0.0247	0.0134
16mm, LIBS	0.3134	0.2324	0.8016	n.d.	n.d.
16mm, EDXRF	n.d.	0.2635	0.8007	0.0247	0.0128
20mm, OES	0.3001	0.2396	0.7932	0.0227	0.0127
20mm, LIBS	0.3033	0.2334	0.8051	n.d.	n.d.
20mm, EDXRF	n.d.	0.2528	0.8059	0.0194	0.0103
25mm, OES	0.3059	0.2536	0.7656	0.0041	0.0165
25mm, LIBS	0.3034	0.2513	0.7653	n.d.	n.d.
25mm, EDXRF	n.d.	0.2155	0.787	0.0069	0.0155
28mm, OES	0.3148	0.2906	0.8135	0.0187	0.0147
28mm, LIBS	0.31	0.3122	0.8303	n.d.	n.d.
28mm, EDXRF	n.d.	0.3221	0.8008	0.0171	0.0174
32mm, OES	0.3356	0.2407	0.8326	0.0282	0.0292
32mm, LIBS	0.3287	0.2471	0.8401	n.d.	n.d.
32mm, EDXRF	n.d.	0.2197	0.8391	0.028	0.0273
36mm, OES	0.3102	0.2962	0.8011	0.0095	0.0133
36mm, LIBS	0.3143	0.2599	0.825	n.d.	n.d.
36mm, EDXRF	n.d.	0.2657	0.8263	0.007	0.0133
40mm, OES	0.2991	0.2582	0.804	0.0281	0.0192
40mm, LIBS	0.3096	0.2358	0.7851	n.d.	n.d.
40mm, EDXRF	n.d.	0.3265	0.7948	0.0173	0.019
50mm, OES	0.3049	0.2201	1.0411	0.0094	0.0296
50mm, LIBS	0.3009	0.2203	1.0587	n.d.	n.d.
50mm, EDXRF	n.d.	0.2393	1.0012	0.003	0.0281

n.d. – not detected

Linear regression coefficient of determination, R^2, Equation 3 was calculated to evaluate the goodness fit of the model Pearson's correlation and linear regression coefficient of determination were calculated using Microsoft Excel data analysis tool. Data were also regressed to find the best-fitting straight line that describes the linear relationship between the two analytical methods following Equation 3.

C. Correlation analysis between Spark-OES, EDXRF, and LIBS

The correlation between Spark-OES and handheld analyzers (EDXRF and LIBS) for elemental analysis of deformed steel bars was evaluated through scatter plots, linear regression, and Pearson's correlation coefficients (r_{xy}), with the results summarized in Figures 4 to 6. For EDXRF, strong positive correlations with Spark-OES were observed for Si and Mn (**Figure 3**).

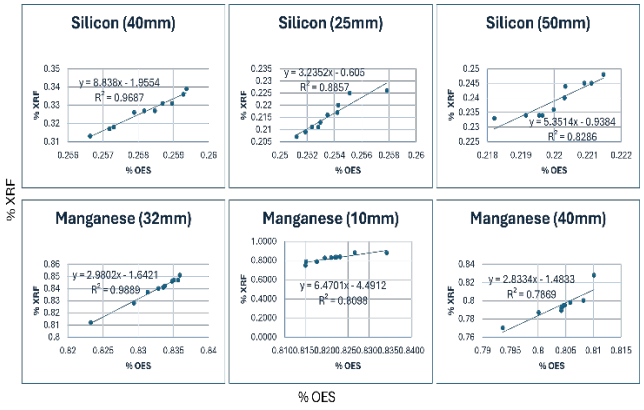

***Fig. 3**. Correlation between OES and EDXRF in the elemental analysis of rebar.*

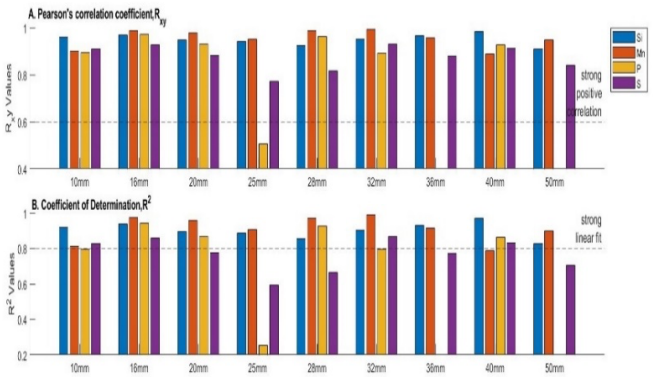

***Fig. 4**. Statistical correlation between OES and EDXRF: (a.) r_{xy}, and (b.) R^2*

Pearson's r_{xy} values for Si ranged from approximately 0.91 to 0.97, with corresponding R^2 values mostly above 0.85, indicating that a large proportion of the variance in EDXRF measurements could be explained by Spark-OES (**Figure 4**).

Similarly, Mn demonstrated high r_{xy} values between 0.90 and 0.99 and R^2 values exceeding 0.90 across different rebar diameters. S exhibited moderate to strong correlations, with r_{xy} values ranging from 0.66 to 0.93 and R^2 generally above 0.65. In contrast, P showed more variable results, with r_{xy} values between 0.49 and 0.80 and lower R^2 values from 0.25 to 0.64, indicating weaker linear relationships.

Comparative analysis between Spark-OES and handheld LIBS also demonstrated strong positive correlations for C, Si, and Mn. Representative scatter plots in **Figure 5** show regression equations and R^2 values across different rebar sizes. Pearson's r_{xy} values for C ranged from 0.819 to 0.982, with R^2 values generally above 0.810. Similarly, for Si, r_{xy} ranged from 0.907 to 0.988 and R^2 exceeded 0.821, confirming strong linearity. Mn correlations ranged from 0.807 to 0.928 for r_{xy}, with R^2 values mostly above 0.697, indicating a consistent positive relationship. Interpretations of correlation strength were adapted from Chan et al. (2003) [13]

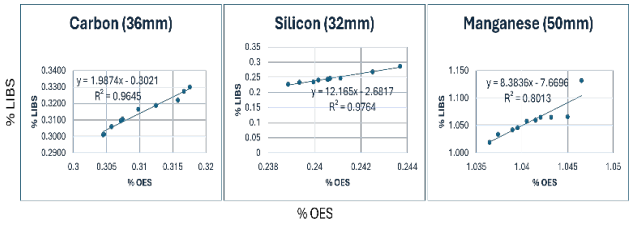

***Fig. 5**. Correlation between OES and LIBS in the elemental analysis of different sizes of rebar*

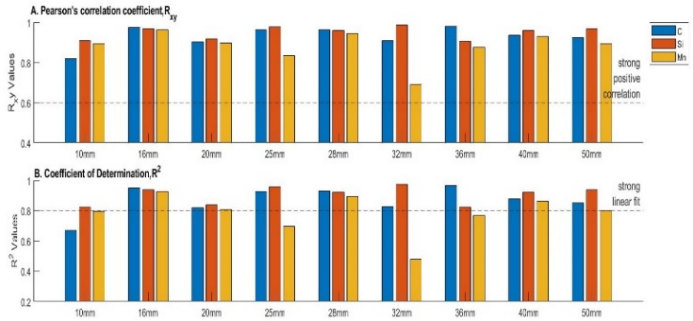

***Fig. 6**. Statistical correlation between OES and LIBS: (a.) r_{xy}, and (b.) R^2*

As shown in **Figure 6**, despite a few cases of moderate

correlations—such as C at 10 mm and Mn at 25 mm and 32 mm diameters—the majority of elements across different sizes exhibited strong agreement. The results confirm that handheld EDXRF and LIBS methods show strong and consistent positive correlations with Spark-OES for key alloying elements. EDXRF is highly reliable for Si and Mn, while LIBS demonstrates robust performance for C, Si, and Mn, supporting the feasibility of these portable techniques for rapid, non-destructive quality control of deformed steel bars.

IV. CONCLUSION

This study evaluated the use of portable analytical techniques—EDXRF and LIBS—for the rapid monitoring of key alloying elements (carbon, silicon, manganese, phosphorus, and sulfur) in deformed steel bars, comparing their performance against the established Spark-OES method. The results demonstrated that LIBS achieved strong positive correlations with Spark-OES for carbon, silicon, and manganese, while EDXRF showed effective correlation particularly for silicon and manganese, highlighting their potential for rapid, on-site quality control applications.

However, limitations were identified in the detection of phosphorus and sulfur using EDXRF. Both the Certified Reference Materials (CRMs) and rebar sample analyses consistently showed that measurement results for these elements require further optimization. Limitations in the detection of phosphorus and sulfur were evident, primarily due to their low atomic numbers, weak fluorescence signals, spectral interferences, and the influence of surface roughness, which may also affect the measurement accuracy. These challenges emphasize the need for enhanced calibration strategies, matrix-matched standards, or the use of vacuum or helium-flushed systems to improve sensitivity and reliability for low-concentration elements.

The findings confirm that handheld LIBS and EDXRF analyzers can serve as viable alternatives or complementary tools to Spark-OES for rapid alloying element analysis in steel bars. With further development to address limitations in phosphorus and sulfur detection, these portable methods can significantly strengthen quality assurance measures in the steel industry and contribute to safer, more reliable infrastructure development.

REFERENCES

[1] W. S. in F. 2023, “World Steel Association.”

[2] R. O. Leramo, L. Adekoya, O. Kilanko et al., “A comparative analysis of the chemical composition and compliance level to established standards of concrete reinforcement steel rods rolled in Nigeria,” Heliyon, vol. 8, no. 6, p. e09597, 2022, doi: 10.1016/j.heliyon.2022.e09597.

[3] J. Odusote, W. Shittu, A. Adeleke, P. Ikubanni, and Adeyemo, “Chemical and Mechanical Properties of Reinforcing Steel Bars from Local Steel Plants,” J. Fail. Anal. Prev., vol. 19, no. 4, pp. 1067–1076, 2019, doi: 10.1007/s11668-019-00695-x.

[4] DTI-BPS Technical Committee 11 - Long Steel Products, “Steel Bars for Concrete Reinforcement – Specification. Philippine National Standard, PNS 49: 2020,” 2020.

[5] T. Fente and A. Tsegaw, “Environmental impact assessment of steel reinforcing bar manufacturing process from scrap materials using life cycle assessment method: a case study on the Ethiopian metal industries,” Discov. Appl. Sci., vol. 6, no. 2, 2024, doi: 10.1007/s42452-024-05709-4.

[6] A. Bengtson, “LIBS compared with conventional plasma optical emission techniques for the analysis of metals – A review of applications and analytical performance,” Spectrochim. Acta - Part B At. Spectrosc., vol. 134, no. June 2017, pp. 123–132, 2017, doi: 10.1016/j.sab.2017.05.006.

[7] M. A. Al-Eshaikh and A. Kadachi, “Elemental analysis of steel products using X-ray fluorescence (XRF) technique,” J. King Saud Univ. - Eng. Sci., vol. 23, no. 2, pp. 75–79, Jun. 2011, doi: 10.1016/j.jksues.2011.03.002.

[8] D. Luo, Y. Liu, X. Li, Z. Zhao, S. Wang, and Y. Zhang, “Quantitative analysis of C, Si, Mn, Ni, Cr and Cu in low-alloy steel under ambient conditions via laser-induced breakdown spectroscopy,” Plasma Sci. Technol., vol. 20, no. 7, 2018, doi: 10.1088/2058-6272/aabc5d.

[9] A. Bengtson, “LIBS compared with conventional plasma optical emission techniques for the analysis of metals – A review of applications and analytical performance,” Spectrochim. Acta - Part B At. Spectrosc., vol. 134, no. June 2017, pp. 123–132, 2017, doi: 10.1016/j.sab.2017.05.006.

[10] P. Seidel, D. Ebert, R. Schinke et al., “Comparison of Elemental Analysis Techniques for the Characterization of Commercial Alloys,” Metals (Basel)., vol. 11, no. 5, p. 736, 2021, doi: 10.3390/met11050736.

[11] K. Mejía-Piña, M. Huerta-Diaz, and O. González-Yajimovich, “Calibration of handheld X-ray fluorescence (XRF) equipment for optimum determination of elemental concentrations in sediment samples,” Talanta, vol. 161, pp. 359–367, 2016, doi: 10.1016/j.talanta.2016.08.066.

[12] AOAC, “Appendix F: Guidelines for Standard Method Performance Requirements,” AOAC Off. Methods Anal., pp. 1–17, 2016.

[13] Chan YH. Biostatistics 104: correlational analysis. Singap Med J. 2003;44(12):614–619.