



Quantitative and Qualitative Analysis of Heavy Trace Metals in Crude Oil from Southern Iraqi Oilfields Using LIBS

Maryam Neamah Saleh^{1*} Sahib Neamah AbdulWahid²

Department of Physics, College of Education, University of kufa , IRAQ²¹,

*Corresponding Author E-mail: maryamneamah.alkufa.university@gmail.com

ARTICLE INF.

Article history:

Received: 10 APR., 2026
Revised: 18 MAY., 2026
Accepted: 23 JUN., 2026
Available Online: 28 JUN.
2026

Keywords:

LIBS,
Heavy Trace Metals,
Iraqi Crude Oil,
Geochemical
Fingerprinting,
Quantitative Analysis,
Reservoir
Characterization

ABSTRACT

The determination of heavy trace metals in crude oil is essential for evaluating environmental risks and refining efficiency. This study investigates the qualitative and quantitative distribution of heavy trace metals in crude oil from major southern Iraqi oilfields (North Rumaila, Majnoon, and Zubair) using Laser-Induced Breakdown Spectroscopy (LIBS). The liquid crude oil samples were thermally treated at 350 °C to produce a stable solid residue, which was then ground into a fine powder and compressed into pellets for LIBS analysis. To achieve efficient material ablation, the laser beam from a Q-switched Nd:YAG laser (1064 nm, 300 mJ, 8 ns) was focused onto the pellet surface using a 50 mm focal length lens. This setup created a focal spot diameter of approximately 0.4 mm, resulting in a calculated laser fluency of 238.8 J/cm² at the target surface. The generated plasma light was then collected and analyzed using an Ocean Optics HR4000CG-UV-NIR spectrometer, equipped with a Toshiba TCD1304AP linear CCD array detector (3648 pixels) covering a spectral range of 200–790 nm. Finally, elemental identification and spectral consistency were verified using the NIST atomic spectra database. A wide range of toxic and radioactive elements (Hg, Pb, Cd, U, Ra) along with transition and noble metals (W, Sn, Mo, Ag, Pt, Au, Ir, Rh) were successfully identified. Quantitative analysis showed strong linearity (R² up to 0.9961), low detection limits (as low as 0.001841% for Pb), and acceptable precision (RSD < 6%). Elemental distribution revealed significant variability, with Hg (6.03–9.65%) and Pb (2.26–6.87%) as dominant contaminants, and pronounced enrichment in the Zubair sample (W3). These findings confirm that LIBS is a rapid, sensitive, and reliable technique for multi-element analysis in crude oil. The observed distribution of heavy trace metals highlights their environmental and industrial significance, particularly in pollution monitoring and refining processes, and demonstrates the potential of LIBS as an effective tool for petroleum characterization and geochemical assessment.

DOI: <https://doi.org/10.31257/2018/JKP/2026/v18.i1.23793>

التحليل الكمي والنوعي للعناصر المعدنية الثقيلة النزرة في النفط الخام من الحقول النفطية في جنوب العراق باستخدام تقنية (LIBS)

مريم نعمه صالح¹, صاحب نعمه عبد الواحد²

^{1,2} قسم الفيزياء , كلية التربية للبنات , جامعة الكوفة , العراق

الخلاصة

الكلمات المفتاحية:

يُعد تحديد العناصر المعدنية الثقيلة النزرة في النفط الخام أمراً أساسياً لتقييم المخاطر البيئية وكفاءة عمليات التكرير. تستقصى هذه الدراسة التوزيع النوعي والكمي للعناصر المعدنية الثقيلة النزرة في النفط الخام من الحقول النفطية الرئيسية في جنوب العراق (شمال الرميلة، مجنون، والزبير) باستخدام تقنية التحليل الطيفي بالانهيبار المستحث بالليزر (LIBS).

،IBS

العناصر المعدنية الثقيلة
النزرة،

تمت معالجة عينات النفط الخام السائل حرارياً عند درجة حرارة 350 درجة مئوية لإنتاج متبق صلب مستقر، جرى طحنه بعد ذلك إلى مسحوق ناعم وضغطه في هيئة أقراص (Pellets) لتحليلها بواسطة تقنية مطيافية الانبعاث الذري المستحث بالليزر (LIBS). ولتحقيق استئصال فعال للمادة، تم تركيز شعاع الليزر من نظام (Q-switched Nd:YAG) بطول موجي 1064 نانومتر، وطاقة 300 ميلي جول، ونبضة مدتها 8 نانو ثانية، على سطح القرص باستخدام عدسة ذات بعد بؤري قدره 50 ملم؛ وقد نتج عن هذا الإعداد بقعة بؤرية بقطر تقريبي يبلغ 0.4 ملم، مما أدى إلى فيض ليزري محسوب قدره 238.8 جول/سم² عند سطح الهدف. جُمع ضوء البلازما المتولد وحُلل باستخدام مطياف (Ocean Optics HR4000CG-UV-NIR)، المزود بكاشف مصفوفة (CCD) خطي من نوع (Toshiba TCD1304AP) بـ 3648 بكسل، يغطي نطاقاً طيفياً يمتد من 200 إلى 790 نانومتر؛ وفي الختام، تم التحقق من تحديد العناصر واتساق الأطياف بالاستناد إلى قاعدة بيانات المعهد الوطني للمعايير والتقنية (NIST) للأطياف الذرية.

النفط الخام العراقي،

البصمة الجيوكيميائية،

التحليل الكمي،

توصيف الأماكن النفطية.

تم التعرف بنجاح على نطاق واسع من العناصر السامة والمشعة (Ra، U، Cd، Pb، Hg) إلى جانب الفلزات الانتقالية والنيبلية (Rh، Ir، Au، Pt، Ag، Mo، Sn، W)، أظهر التحليل الكمي خطية عالية (معامل تحديد R^2 يصل إلى 0.9961)، وحدود كشف منخفضة (تصل إلى 0.001841% لمعدن Pb)، ودقة مقبولة ($RSD < 6\%$)، وكشف توزيع العناصر عن تباين ملحوظ، حيث كان الزئبق Hg (6.03–9.65%) والرصاص Pb (2.26–6.87%) من الملوثات السائدة، مع إغناء واضح في عينة الزبير (W3).

تؤكد هذه النتائج أن تقنية LIBS تُعد وسيلة سريعة وحساسة وموثوقة لتحليل متعدد العناصر في النفط الخام. كما يبرز التوزيع الملحوظ للعناصر المعدنية الثقيلة النزرة أهميتها البيئية والصناعية، ولا سيما في مراقبة التلوث وعمليات التكرير، ويُظهر الإمكانيات الكبيرة لتقنية LIBS كأداة فعالة في توصيف النفط والتقييم الجيوكيميائي.

1. INTRODUCTION

Crude oil is a vital natural resource underpinning global economic and

industrial development, serving as a primary source of energy and petrochemical feedstock [1]. It also constitutes a cornerstone of the Iraqi economy, accounting for approximately 96% of total exports and significantly influencing GDP, national income, and foreign reserves [2].

Chemically, crude oil is a complex mixture of hydrocarbons along with non-hydrocarbon compounds containing sulfur, nitrogen, and oxygen, in addition to trace levels of rare earth elements [3]. Heavy metals, particularly nickel (Ni), vanadium (V), iron (Fe), cobalt (Co), and copper (Cu), form an important fraction of its inorganic composition. Despite their low concentrations, these metals strongly influence oil properties and are commonly associated with complex molecular structures such as porphyrins, exhibiting distinct spectral behavior in laser-induced plasmas [4].

Heavy metals play a crucial role in petroleum geochemistry as indicators of oil type, origin, and thermal maturity, while their elevated levels pose industrial challenges by deactivating refining catalysts and increasing emissions. Therefore, rapid and accurate detection is essential. Laser-Induced Breakdown Spectroscopy (LIBS) provides a powerful analytical approach for direct multi-element detection, offering advantages over conventional techniques such as ICP-MS and AAS in terms of minimal sample preparation and faster analysis. LIBS operates by generating plasma through laser ablation and

analyzing emitted spectra for qualitative and quantitative determination [5–9].

LIBS enables real-time, in-situ elemental analysis with high sensitivity and multi-element capability, supporting applications across environmental monitoring, industrial analysis, and petroleum studies [10–15]. Previous studies have demonstrated its effectiveness in detecting heavy metals in crude oil, including improvements in sensitivity and homogeneity using advanced sample preparation methods such as xerogels and thin films [16,20].

However, a significant research gap remains regarding the scarcity of comprehensive studies addressing Iraqi crude oil using LIBS in a direct and integrated manner. The scientific literature lacks extensive research that combines precise qualitative and quantitative analysis of both heavy metals and radioactive elements, which may be present in varying concentrations and impact both oil quality and environmental safety [21, 22].

This study specifically aims to bridge this gap by developing a comprehensive LIBS-based analytical framework to determine the concentration of trace heavy metals and potentially radioactive constituents in crude oil samples from key southern Iraqi oilfields. A primary objective is to critically evaluate the efficiency and precision of LIBS in comparison to traditional techniques (such as ICP-OES/MS), establishing its reliability for

industrial grade analysis. Additionally, the research seeks to explore the geochemical disparities and elemental distributions across these fields, providing new insights into the correlation between inorganic trace profiles and the geological characteristics of the southern Iraqi petroleum reservoirs [23-25]

LIBS ANALYTICAL FEATURES

Laser-Induced Breakdown Spectroscopy (LIBS) enables the detection of a wide range of elements across the periodic table, from hydrogen (H) to uranium (U). However, its analytical performance is influenced by factors such as ionization energy and matrix effects, which may reduce sensitivity for certain light elements (e.g., B, Li, Be). In contrast, transition and heavy metals such as Fe, Cu, Pb, and Zn are typically quantified with higher reliability. LIBS has also demonstrated effectiveness in detecting toxic metals including As, Cd, and Hg [26,27].

In compared to conventional analytical methodologies, Laser-Induced Breakdown Spectroscopy (LIBS) demonstrates a superior elemental detection gamut. While Instrumental Neutron Activation Analysis (INAA) exhibits high sensitivity for a broad spectrum of elements (Na to U), and X-ray Fluorescence (XRF) remains limited to the F-U range with significant constraints in light element detection, LIBS facilitates the identification of nearly the entire periodic table, including low-Z elements. Furthermore, in contrast to X-ray Photoelectron Spectroscopy (XPS), which is inherently surface-

confined to nano-metric depths, LIBS provides a more comprehensive analytical volume through its multi-pulse ablation capabilities. Consequently, the capacity for rapid, multi-elemental acquisition without extensive sample pretreatment renders LIBS a more robust and versatile candidate than XRF for the characterization of complex hydrocarbon matrices such as crude oil [28–30].

The analytical accuracy of LIBS ranges from moderate to high, depending on matrix effects, environmental conditions, and calibration procedures, with reliable quantification requiring appropriate reference standards [31]. Precision typically falls within a relative standard deviation (RSD) of 5–10% [32]. LIBS exhibits ppm-level sensitivity, with detection limits generally in the tens to hundreds of ppm, which can be improved through optimized conditions or advanced approaches such as double-pulse configurations [33–34].

Although LIBS generally shows lower sensitivity and higher detection limits than ICP and INAA, it offers significant advantages, including rapid analysis, minimal sample preparation, and in-situ capability, making it highly suitable for real-time and field-based applications [35].

3. EXPERIMENTAL METHODOLOGY

3.1 Sample Collection

Crude oil samples were collected from major southern Iraqi oil fields (North Rumaila, Zubair, and Majnoon) to investigate the distribution of trace heavy metals using spectroscopic techniques. Standard sampling procedures were

strictly followed to ensure representativeness and to minimize contamination during collection, handling, and transportation. Samples were transferred into clean, chemically inert containers to preserve their original composition. The selected fields provide geological diversity, enhancing the

reliability of the analysis. All samples were coded as “W,” as presented in Table 1.

Table 1: Names and Locations of Crude Oil Samples Analyzed in this Study

Sample	Name Field	Governorate	Region
W1	North Rumaila	Basra	South Iraq
W2	Majnoon	Basra	South Iraq
W3	Zubair	Basra	South Iraq

3.2 Sample preparation

To ensure reliable LIBS analysis, crude oil samples were thermally treated to obtain solid residues. For each sample, 10 mL of crude oil was heated at 350 °C under atmospheric conditions to remove volatile components, and the process was repeated five times to obtain sufficient material. The resulting residues were ground using an agate mortar to produce a homogeneous fine powder (<0.5 mm). Approximately 0.25 g of the powder was then compressed into pellets (10 mm diameter, ~1 mm thickness) at 20 MPa using a hydraulic press. These preparation steps improve sample homogeneity, reduce matrix effects, enhance spectral quality, and minimize the influence of moisture on LIBS signal intensity [36–38].

3.3 LIBS Technology

Laser-Induced Breakdown Spectroscopy (LIBS) is an atomic emission technique derived from AES, utilizing high-energy laser pulses as an excitation source for multi-elemental analysis [39]. A typical LIBS system consists of a laser source, beam delivery optics, plasma emission collection components, a spectrometer, and a detection unit.

In this study, a Q-switched Nd:YAG laser (1064 nm, 300 mJ, 8 ns, 6 Hz) was employed to induce plasma on the surface of solid crude oil samples. The laser beam was focused using a 50 mm focal length lens, producing a focal spot diameter of approximately 0.4 mm and a calculated laser fluence of 238.8 J/cm². The resulting plasma emission was collected at a 90° geometry via a collimating lens and transmitted through a fused silica optical fiber to an Ocean Optics HR4000CG-UV-NIR

spectrometer equipped with a Toshiba TCD1304AP linear CCD detector, providing spectral coverage from 200 to 790 nm with a spectral stability of 0.1 nm (Fig. 1).

For each pellet, spectra were acquired from different surface positions to minimize local inhomogeneity effects. Each reported spectrum represented the average of 20 accumulated laser shots, while the measurement was repeated **three** times under identical experimental conditions to improve repeatability and signal stability. Prior to spectral acquisition, preliminary cleaning shots were applied to remove possible surface contamination. Instrument calibration was verified using standard reference emission lines to ensure wavelength accuracy and spectral reproducibility throughout the measurements.

The analytical capability of LIBS is based on the identification and quantification of elements through their characteristic emission lines [40]. Nanosecond laser pulses were selected due to their stable plasma generation and balanced analytical performance. In addition, synchronization between the laser pulse and detector through an optimized delay time significantly improved the signal-to-background ratio and enhanced analytical precision.

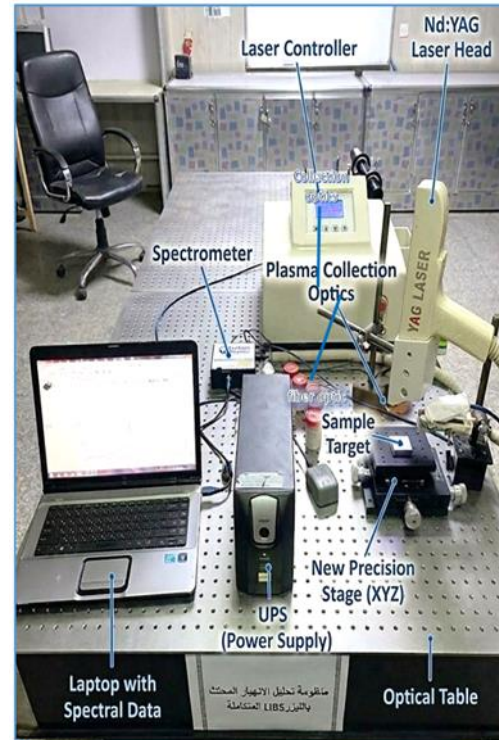


Fig. 1. The experimental setup of Laser Induced Breakdown Spectroscopy (LIBS).

3.4 Plasma Evolution

The evolution of LIBS plasma involves a sequence of rapid physical processes, beginning with surface heating, followed by melting, vaporization, and ionization. Upon irradiation with a high-energy laser pulse, a small quantity of material (on the order of micrograms) is ablated, leading to the formation of a transient plasma composed of atoms, ions, and electrons [41].

The plasma reaches very high temperatures and expands rapidly away from the sample surface, followed by a cooling phase during which continuum emission decreases and characteristic atomic emissions become dominant. These emissions, corresponding to

specific elemental wavelengths, form the basis of LIBS analysis.

The emitted radiation is collected and directed to a spectrometer equipped with a CCD detector, enabling high-resolution spectral acquisition typically within the 200–790 nm range. Spectral resolution is a key factor in distinguishing closely spaced emission lines, particularly in complex matrices such as crude oil. Elemental identification is achieved by comparing measured wavelengths with standard reference data, such as the NIST database.

4. RESULTS AND DISCUSSION

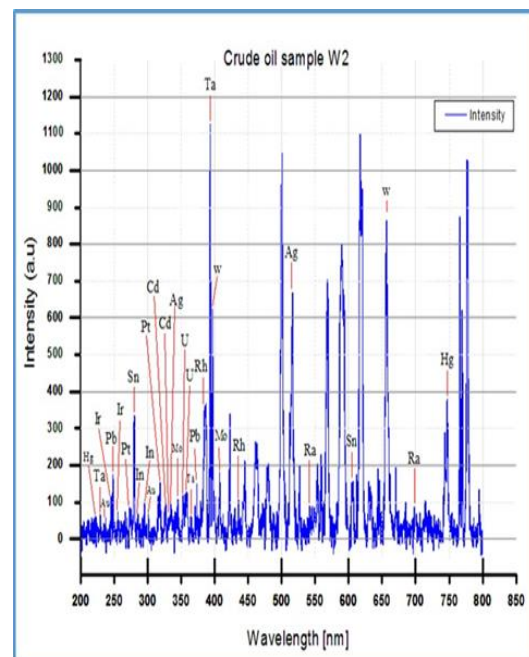
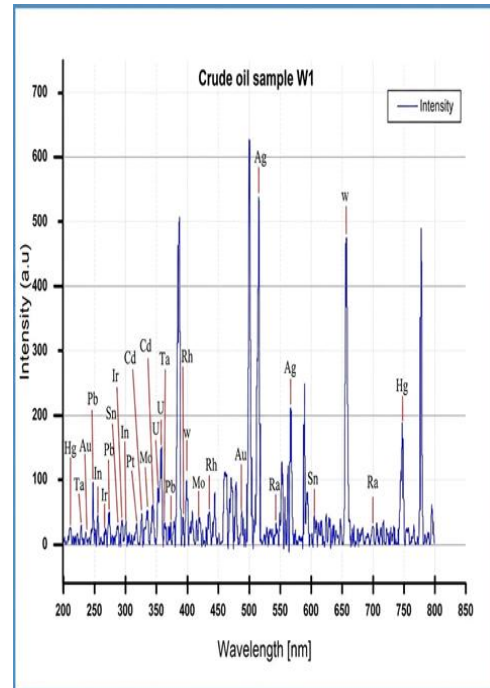
4.1 Qualitative Analysis of Heavy Trace Metals

The LIBS spectra of crude oil samples (W1–W3) within the 200–790 nm range exhibited characteristic emission profiles consisting of a continuum background with superimposed sharp atomic lines, enabling direct qualitative elemental identification. Spectral lines were accurately matched with the NIST database, ensuring reliable identification, as shown in Fig.2. (a, b, c).

The analysis confirmed the presence of several heavy trace metals, including Hg, Cd, Pb, U, Ra, Mo, Sn, W, Ta, and In, detected through low-intensity emission lines consistent with their trace concentrations. Their identification reflects the high sensitivity of LIBS for multi-element detection in complex matrices. Additionally, noble metals such as Ag, Pt, Au, Ir, and Rh were detected, demonstrating the capability of LIBS to identify elements with high

ionization energies and weak emission characteristics.

More abundant elements, including V, Ni, Fe, Cu, Zn, Cr, Mn, Co, Ti, Sr, and Ba, exhibited stronger emission lines, highlighting the wide dynamic range and robustness of LIBS for simultaneous detection of major and trace elements.



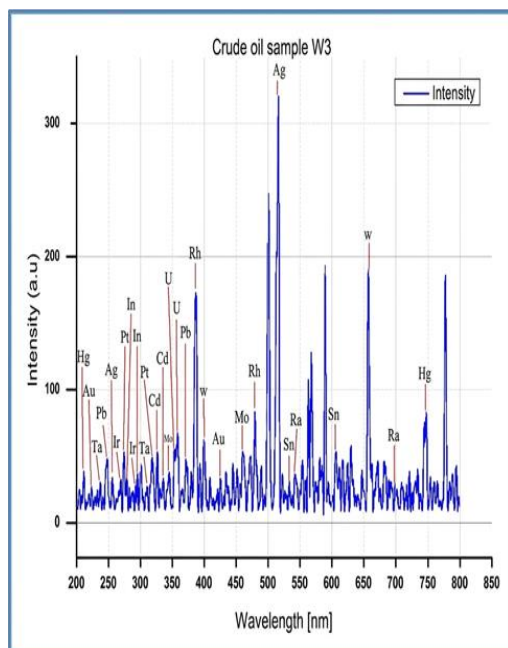


Fig 2. Typical LIBS spectra of crude oil samples W1 (North Rumaila), W2 (Majnoon) and W3 (Zubair), collected from southe Iraqi oil fields, recorded in the 200–790 nm range. Variations in LIBS signal intensity along the y-axis reflect differences in the concentrations of Heavy trace metals present in each sample.

4.2 Quantitative Analysis of Iraqi Crude Oil Samples Using LIBS

The quantitative performance of LIBS for heavy trace metal analysis in Iraqi crude oil was evaluated using LOD, LOQ, RSD, and R^2 (Table 2).

The quantitative accuracy is based on the LOD equation

$$LOD = \frac{3\sigma}{S}$$

where σ is the background standard deviation and S is the calibration sensitivity.

Excellent linearity was achieved for all elements, with R^2 values ranging

from 0.9776 to 0.994, confirming the reliability of the calibration models.

LOD values showed element-dependent variation, with the lowest values obtained for Pb (0.001841%), U (0.001986%), and Mo (0.006822%), indicating high sensitivity, while higher LODs for Sn (0.143353%) and Hg (0.634028%) reflect weaker emission efficiency and plasma-related effects. LOQ values followed a similar trend, further supporting the variability in quantification capability.

The method demonstrated good precision, with RSD values between 1.167% and 5.755%, indicating acceptable repeatability for complex matrices. Lower RSD values (e.g., W, Rh) suggest stable plasma conditions, whereas higher values (e.g., U) may be attributed to matrix effects and signal fluctuations.

Overall, LIBS exhibits reliable quantitative performance for multi-element detection, with sensitivity and accuracy governed by elemental spectroscopic properties and plasma dynamics, confirming its suitability for rapid analysis of heavy trace metals in crude oil [42].

Although direct experimental validation using reference techniques such as ICP-MS or AAS was not performed due to instrumental limitations, the obtained LIBS results demonstrated high linearity (R^2 up to 0.9961), low detection limits, and acceptable repeatability (RSD < 6%). Furthermore, the detected elemental distribution patterns and concentration trends showed good consistency with

previously reported spectroscopic studies on crude oil residues and petroleum matrices [43,44]. These observations support the reliability of the proposed LIBS methodology for rapid multi-element analysis of Iraqi crude oil samples.

Table (2): Analytical performance parameters of trace heavy metals identified by LIBS in Iraqi crude oil samples.

ELEMENT	λ	LOD(%)	LOQ(%)	RSD	R^2
Sn	606.91	0.14335	0.47306	4.73066	0.9781
W	660.90	0.03539	0.11678	1.16789	0.9912
Ag	514.28	0.27706	0.91431	4.14311	0.9797
Cd	325.03	0.01931	0.06374	2.37444	0.9868
Pb	247.63	0.00184	0.00607	2.07676	0.9898
U	356.87	0.00198	0.00655	5.75466	0.9923
Ra	540.67	0.01279	0.04223	4.18340	0.9799
Pt	315.90	0.00921	0.03039	2.99951	0.9859
In	280.79	0.01357	0.04479	4.43984	0.9961
Ir	252.36	0.01453	0.04796	4.75682	0.9942
Ta	362.66	0.00688	0.02271	2.23128	0.9776
Mo	350.81	0.00682	0.02251	2.21112	0.9785
Rh	391.35	0.00517	0.01709	1.66902	0.9868
Au	235.25	0.00480	0.01584	1.54489	0.9874
Hg	320.80	0.63402	2.09229	1.89229	0.9799

4.3 Distribution of Heavy Trace Metal Concentrations in Iraqi Crude Oil

Table (3) presents the concentrations (%) of heavy trace metals in crude oil samples from southern Iraqi oilfields (Rumaila, Majnoon, and Zubair), revealing clear variability in elemental distribution.

Mercury (Hg) exhibited the highest concentrations, ranging from 6.03% (Majnoon) to 9.65% (Zubair), followed by lead (Pb) (2.26–6.87%) with a clear enrichment in Zubair.

The relatively elevated Hg and Pb values obtained in the present study

compared with commonly reported concentrations in global crude oil matrices may be attributed to several analytical and physicochemical factors associated with LIBS measurements and sample preparation procedures. During the thermal treatment process at 350 °C, volatile hydrocarbon fractions were removed, which may have resulted in the relative enrichment of non-volatile heavy metallic constituents within the remaining solid residues subjected to LIBS analysis. Similar enrichment behavior following thermal concentration has been discussed in previous spectroscopic investigations of petroleum residues and hydrocarbon-derived matrices [45].

In addition, quantitative LIBS analysis of complex petroleum samples is strongly influenced by matrix effects, plasma temperature fluctuations, self-absorption phenomena, and spectral line overlap, all of which can alter emission intensities and affect the apparent elemental concentrations [46,47]. The heterogeneous composition of crude oil residues, containing both organic and inorganic phases, may further contribute to variations in laser–matter interaction and plasma expansion dynamics.

Despite these limitations, several indicators support the internal reliability and reproducibility of the obtained results. The measurements demonstrated acceptable repeatability with relative standard deviation (RSD) values below 6%, high calibration linearity (R^2 up to 0.9961), and stable spectral behavior across repeated acquisitions performed at different pellet positions. Therefore, the reported values should be interpreted primarily

as relative quantitative distributions within the analyzed solid residues rather than absolute bulk concentrations of untreated crude oil samples. Further validation using complementary analytical techniques such as ICP-MS or AAS is recommended to confirm absolute concentration levels.

Similarly, tungsten (W) reached its maximum in Rumaila (6.24%), while tin (Sn) remained relatively stable (~2.52–3.43%) across all fields.

Moderate concentrations were observed for Au and Rh, both showing a clear increasing trend toward Zubair (Au: 0.02 → 1.74%, Rh: 0.14 → 1.36% from Rumaila to Zubair). Silver (Ag) also exhibited a strong increasing trend (0.006% in Rumaila to 1.50% in Zubair), indicating progressive enrichment.

Radioactive elements showed distinct behavior, with U peaking in Majnoon (1.86%), while Ra increased toward Zubair (0.55%), suggesting variable distribution patterns among fields. In contrast, Pt displayed a localized maximum in Majnoon (1.71%), unlike most elements.

Lower concentrations were consistently observed for Mo, Ta, In, Ir, and Cd, with no clear enrichment trend, confirming their trace-level presence.

Overall, a general enrichment trend is observed toward Zubair for most elements (Hg, Pb, Au, Rh, Ag, Ra), while Majnoon shows localized enrichment in specific elements (U, Pt), and Rumaila is characterized by relatively lower concentrations except for W. These trends highlight

compositional heterogeneity among the oilfields and reflect differences in plasma–element interaction and matrix effects during LIBS analysis [43].

These findings regarding the characterization and distribution of heavy metal elements reinforce the conclusions of previous spectroscopic studies conducted on various hydrocarbon residues. The high degree of consistency with references [48, 49] confirms the effectiveness of the LIBS technique as a precise analytical tool for monitoring trace elements and its superior capability to track concentration gradients within complex petroleum matrices, thereby providing additional reliability to the elemental variations recorded in the current study.

The relatively high Hg and Pb values observed in the Zubair sample compared with commonly reported global crude oil concentrations may be related to both geological and analytical factors. Variations in source rock composition, reservoir maturity, and industrial activities associated with oil production may contribute to localized heavy metal enrichment [46]. In addition, thermal treatment of crude oil prior to LIBS analysis may lead to relative enrichment of non-volatile metallic constituents within the analyzed residues [49]. From an analytical perspective, matrix effects, plasma fluctuations, self-absorption, and spectral overlap can significantly influence LIBS emission intensities and quantitative estimations [49]. Nevertheless, the acceptable repeatability (RSD < 6%) and high calibration linearity (R^2 up to 0.9961)

support the reproducibility and relative quantitative reliability of the obtained results.

Table (3): Relative Quantitative Concentrations (%) of trace heavy metals in Iraqi crude oil residues determined by LIBS.

Element	W1	W2	W3
Sn	3.416654053	2.523782194	3.425958688
W	6.237032441	3.537753263	3.938661929
Ag	0.006034686	0.256858893	1.504430726
Cd	0.008781801	0.147418592	0.121261391
Pb	4.734605802	2.259490649	6.871674699
U	1.665306491	1.855755791	0.330820311
Ra	0.081990293	0.287537376	0.552755568
Pt	0.293837496	1.705567061	0.373871134
In	0.085844411	0.539388017	0.009137427
Ir	0.071667988	0.828481337	0.009402715
Ta	0.236123841	0.301579575	0.032449726

Mo	0.395156916	0.314580863	0.02350268
Rh	0.140311768	0.476724181	1.355044647
Au	0.016722206	1.592291754	1.735570486
Hg	7.251584983	6.031536416	9.652437621

5. CONCLUSION

This study confirms the effectiveness of LIBS as a rapid and reliable technique for the qualitative and quantitative analysis of heavy trace metals in crude oil from southern Iraqi oilfields (Rumaila, Majnoon, and Zubair). Multiple heavy trace metals (Hg, Cd, Pb, U, Ra, Mo, Sn, W, Ta, In) and noble metals (Ag, Pt, Au, Ir, Rh) were successfully identified, demonstrating the multi-element detection capability of the technique.

The method showed strong analytical performance, with high linearity ($R^2 = 0.9776-0.994$) and good precision ($RSD < 6\%$). Quantitative results revealed clear variability among fields, with Zubair enriched in most elements (Hg, Pb, Au, Rh, Ag), while Majnoon showed localized enrichment in U and Pt, and Rumaila exhibited generally lower concentrations except for W.

Overall, the results demonstrate that LIBS provides a rapid and reliable approach for multi-element analysis in complex crude oil matrices, with analytical performance supported by acceptable precision, strong calibration linearity, and consistency with

previously reported spectroscopic studies.

6. REFERENCES

1. Speight, J. G. (2014). *The Chemistry and Technology of Petroleum* (5th ed.). CRC Press.
2. Ali, L. A. (2025). The Impact of Oil Revenues on the Gross Domestic Product in Iraq for the Period (2005–2020). *South Asian Res J Bus Manag*, 7(3), 209-217.
3. McIntire, M. C. (2014). *Rare earth elements (REE) in crude oil in the Lansing-Kansas City formations in central Kansas: potential indications about their sources, locally derived or long-distance derived* (Doctoral dissertation, Kansas State University).
4. Speight, J. G. (2014). *The Chemistry and Technology of Petroleum* (5th ed.). CRC Press.
5. Yu K-Q, Zhao Y-R, Liu F, He Y. Laser-induced breakdown spectroscopy coupled with multivariate chemometrics for variety discrimination of soil. *Sci Rep* 2016;6(1):27574.
6. Peng J, Liu F, Zhou F, Song K, Zhang C, Ye L, et al. Challenging applications for multi-element analysis by laserinduced breakdown spectroscopy in agriculture: a review. *TrAC Trends Anal Chem* 2016;85:260e72.
7. Fikry M, Tawfik W, Omar M. Controlling the plasma electron number density of copper metal using NIR picosecond laser-induced plasma spectroscopy. *Opt Appl* 2021;51(3).
8. Fikry M, Tawfik W, Omar M. Measurement of the electron temperature in a metallic copper using ultrafast laserinduced breakdown spectroscopy. *J Russ Laser Res* 2020; 41(5):484e90.
9. Ismail MA, Imam H, Elhassan A, Youniss WT, Harith MAJ. LIBS limit of detection and plasma parameters of some elements in two different metallic matrices. *J Anal At Spectrom* 2004;19(4):489e94.
10. L.J. Redziemsky, T.R. Loree, D.A. Cremers, N.M. Hoffman, *Anal. Chem.* 55 (1983) 1246.
11. D.A. Cremers, L.J. Radziemsky, *Anal. Chem.* 55 (1983) 1252.
12. J. Belliveau, L. Cadwell, K. Coleman, L. Huwel, H. Griffin, *Appl. Spectrosc.* 39 (1985) 727.
13. M. Casini, A. Cucci, M. De Rosa, F. Fama, V. Palleschi, A. Salvetti, D.P. Singh, M. Vaselli, *Opto-laser* 3 (1990) 26.
14. M. Casani, M.A. Harith, V. Palleschi, A. Salvetti, D.P. Singh, M. Vaselli, *Laser Particle Beams* 9 (1991) 633.
15. C. Lazzari, M. De Rosa, S. Rastelli, A. Cucci, V. Palleschi, A. Salvetti, *Laser Part. Beams* 12 (1994) 525.
16. H. Schroeder, I. Schechter, R. Wisbrun, R. Niessner, in: L.D. Laude (Ed.), *Excimer Lasers and Applications*, Kluwer Academic Publishers, The Netherlands, 1994, pp. 269–287.

17. M.A. Khater, J.T. Costello, E.T. Kennedy, *Appl. Spectrosc.* 56 (2002) 970.
18. A. Striganove, N. Sventitski, *Table of Spectral Lines of Neutral and Ionized Atoms*, Plenum, New York, 1968.
19. Y. Lee, K. Song, J. Sneddon, *Laser Induced Breakdown Spectrometry*, Nova Sci. Pub. Inc., New York, 2000.
20. Q. Sun, M. Tran, B.W. Smith, J.D. Winefordner, *Annal. Chim. Acta* 413 (2000) 187
21.] Ahmed, S., et al. (2024). "Current status of elemental analysis in Middle Eastern crude oils: A review of spectroscopic gaps."
22. Al-Maliki, M. J. (2025). "Geochemical mapping of radioactive traces in Iraqi oil reservoirs: Challenges and techniques."
23. Saleh, M. N., et al. "Elemental fingerprinting of crude oil using laser-induced plasma: Challenges and opportunities in the Middle East reservoirs." *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2024.
24. Mao, X., et al. "Comparison of LIBS and ICP-MS for trace metal analysis in heavy hydrocarbons." *Analytical Methods*, 2023.
25. I-Qasim, R. "Spatial distribution of heavy metals in southern Iraqi oil fields: A geochemical perspective." *Iraqi Journal of Science*, 2025 Petroleum Research Center. (2026). "Comparative study of traditional vs. laser-based
26. Khan Z, Ullah MH, Rahman B, Talukder AI, Wahadoszamen M, Abedin K, et al. Laser-induced breakdown spectroscopy (LIBS) for trace element detection: a review. *J Spectrosc* 2022;2022(1):3887038.
27. Thakur SN, Singh JPJL-IBS. *Fundamentals of LIBS and recent developments*. 2020. p. 3e22.
28. Jean-Noëla MK, Arthurb KT, Jean-Marcc B. LIBS technology and its application: overview of the different research areas. *J Environ Sci Public Health* 2020;4(3):134e49.
29. Pathak AK, Kumar R, Singh VK, Agrawal R, Rai S, Rai AK. Assessment of LIBS for spectrochemical analysis: a review. *Appl Spectrosc Rev* 2012;47(1):14e40.
30. Khater MA. Trace detection of light elements by laserinduced breakdown spectroscopy (LIBS): applications to non-conducting materials. *Opt Spectrosc* 2013;115:574e90.
31. Xu X, Du C, Ma F, Shen Y, Zhou J. Fast and simultaneous determination of soil properties using laser-induced breakdown spectroscopy (LIBS): a case study of typical farmland soils in China. *Earth-Sci Rev* 2019;3(4):66.
32. Sun C, Tian Y, Gao L, Niu Y, Zhang T, Li H, et al. Machine learning allows calibration models to predict trace element concentration in soils with

- generalized LIBS spectra. *Sci Rep* 2019;9(1):11363
33. Guo G, Niu G, Shi Q, Lin Q, Tian D, Duan Y. Multi-element quantitative analysis of soils by laser induced breakdown spectroscopy (LIBS) coupled with univariate and multivariate regression methods. *Anal Methods* 2019;11(23):3006e13.
 34. Jantzi SC, Almirall JR. Elemental analysis of soils using laser ablation inductively coupled plasma mass spectrometry (LAICP-MS) and laser-induced breakdown spectroscopy (LIBS) with multivariate discrimination: tape mounting as an alternative to pellets for small forensic transfer specimens. *Appl Spectrosc* 2014;68(9):963e74.
 35. Popov AM, Colao F, Fantoni RJ. Spatial confinement of laserinduced plasma to enhance LIBS sensitivity for trace elements determination in soils. *At Spectrom* 2010;25(6):837e48.
 36. Zhou R, Tang Z, Liu K, Zhang W, Liu K, Li X, et al. High sensitivity analysis of soil by laser-induced breakdown spectroscopy with Ag nanoparticles. *Opt Laser Technol* 2022; 155:108386.
 37. Villas-Boas PR, Franco MA, Martin-Neto L, Gollany HT, Milori DM. Applications of laser-induced breakdown spectroscopy for soil characterization, part II: review of elemental analysis and soil classification. *Eur J Soil Sci* 2020;71(5): 805e18.
 38. Meissner, K., Lippert, T., Wokaun, A., & Günther, D. (2004). Analysis of trace metals in comparison of laser-induced breakdown spectroscopy with LA-ICP-MS. *Thin Solid Films*, 453, 316-322.
 39. Kim G, Kwak J, Kim K-R, Lee H, Kim K-W, Yang H, et al. Rapid detection of soils contaminated with heavy metals and oils by laser induced breakdown spectroscopy (LIBS). *J Hazard Mater* 2013;263:754e60.
 40. Lal B, Zheng H, Yueh F-Y, Singh JP. Parametric study of pellets for elemental analysis with laser-induced breakdown spectroscopy. *Appl Opt* 2004;43(13):2792e7.
 41. Bricklemeyer RS, Brown DJ, Barefield JE, Clegg SM. Intact soil core total, inorganic, and organic carbon measurement using laser-induced breakdown spectroscopy. *Soil Sci Soc Am J* 2011;75(3):1006e18.
 42. Gupta S, Pandotra P, Gupta A, Dhar J, Sharma G, Ram G, et al. Volatile (As and Hg) and non-volatile (Pb and Cd) toxic heavy metals analysis in rhizome of *Zingiber officinale* collected from different locations of North Western Himalayas by Atomic Absorption Spectroscopy. *Food Chem Toxicol* 2010;48(10):2966e71.
 43. Villas-Boas PR, Romano RA, de Menezes Franco MA, Ferreira

- EC, Ferreira EJ, Crestana S, et al. Laser-induced breakdown spectroscopy to determine soil texture: a fast analytical technique. *Geoderma* 2016;263:195e202.
44. Fortes FJ, Moros J, Lucena P, Cabalín LM, Laserna JJ. Laserinduced breakdown spectroscopy. *Anal Chem* 2013;85(2): 640e69.
45. Hahn, D. W., & Omenetto, N. (2012). Laser-Induced Breakdown Spectroscopy (LIBS), Part II: Review of instrumental and methodological approaches. *Applied Spectroscopy*, 66(4), 347–419.
46. Gaudiuso, R., Dell’Aglia, M., De Pascale, O., Senesi, G. S., & De Giacomo, A. (2010). Laser Induced Breakdown Spectroscopy for elemental analysis in environmental, cultural heritage and space applications. *Sensors*, 10(8), 7434–7468.
47. David W. Hahn & Nicolás Omenetto (2012) Laser-Induced Breakdown Spectroscopy (LIBS), Part II: Review of Instrumental and Methodological Approaches to Material Analysis and Applications to Different Fields *Applied Spectroscopy*, 66(4), 347–419.
48. Bilal,A,H., Ahmed,A,A., Abdul Khaliq,F. (2022.) Quality assessment of heavy metals presented in crude oil by identification spectral lines by the LIBS – System.
49. Gondal.M.A., Hussain,T., Yamani,Z,H., Baig,M,A. (2006).Detection of heavy metals in Arabian crude oil residue using laser induced breakdown spectroscopy.