Droplet-based laser ablation ICP-MS for direct elemental screening of oils with minimal sample preparation

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Keywords

LA-ICP-MS, analysis of liquids, oil analysis, elemental analysis

Highlights

Method for rapid multi-element screening of oils.

Internal standardization reduces matrix-induced variability.

Small sample volume and simplified analytical workflow.

193 and 213 nm laser compared for sensitivity and fractionation.

Abstract

A droplet-based laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) method was developed for the direct multi-elemental analysis of oils using minimal sample preparation. Small sample volumes (0.2–10 µL) were deposited onto a flat PTFE substrate and analyzed directly. The influence of key laser ablation parameters, including fluence, repetition rate, number of laser shots, and droplet volume, was systematically investigated.

Under optimized conditions, limits of quantification were in the low µg g^{-1} range for most elements, and repeatability typically remained below 8–10 % when internal standardization (In) was applied. The internal standard significantly reduced matrix-related signal variability. Accuracy was assessed using spiked samples, yielding recoveries within 90–110%, and by comparison with conventional ICP-MS after microwave digestion, showing good agreement between both approaches.

The method was applied to the elemental screening of 20 commercial oil samples. Although not intended for ultra-trace quantification, the proposed approach provides a rapid, low-consumption, and operationally simple alternative for routine multi-element screening of complex oil matrices.

1 Introduction

Elemental analysis of organic liquids is of considerable analytical interest due to their widespread use in industrial, environmental, and technological applications. Among these materials, lubricating and technical oils represent a particularly important class, as their

elemental composition reflects both additive formulation and ongoing mechanical and chemical processes during operation.[1, 2] Moreover, elevated concentrations of certain metals can negatively affect refining operations, contributing to corrosion, catalyst poisoning, and overall deterioration of product quality[3, 4], and the presence of metallic wear particles within the oil serves as an indicator of machinery condition, enabling early detection of mechanical degradation and potential failures[5].

Inductively coupled plasma optical emission spectrometry (ICP-OES)[6-9] and inductively coupled plasma mass spectrometry (ICP-MS)[7, 10-12] are the most widely applied techniques for elemental analysis of oils. the direct introduction of hydrocarbon-rich matrices into the plasma is analytically challenging and may lead to carbon deposition on the spectrometer interface, plasma instability, spectral polyatomic interferences, and non-spectral interferences[11-15]. Direct measurements are possible after dilution with xylene, but this typically requires specialized instrumentation[14], such as a high-temperature torch integrated sample introduction system (hTISIS)[8], direct injection high-efficiency nebulizer (DIHEN)[15], ultrasonic nebulization [13], or solvent-resistant tubing[7], and generally involves complex optimization of pneumatic nebulization conditions[8, 13].

Microwave-assisted acid digestion is thus currently the most established approach, enabling complete decomposition of the organic matrix with acids under elevated temperature and pressure[10, 11, 16]. Nitric acid is typically used, often in combination with H_2O_2[10, 11, 16], while HCl is sometimes included in the process[11]. Alternative decomposition method, microwave-induced combustion (MIC), combines the advantages of acid digestion and combustion by oxidizing the sample in a pressurized oxygen-rich vessel[3, 9]. Liquid–liquid extraction has also been applied[17], with extraction agents including water[18], mineral acids such as HCl and HNO_3[19], chelating agents such as N,N′-bis(4-methoxysalicylidene)-1,2-diaminoethane for Fe and Cu[17], and ionic liquids, which have recently gained popularity[20]. Despite their effectiveness, these techniques are time-consuming and require specialized reagents.

Laser ablation ICP-MS (LA-ICP-MS) offers an attractive alternative for elemental analysis of oils, as it minimizes plasma-related issues associated with high carbon loads and requires only minimal sample preparation. Despite these advantages, the application of LA-ICP-MS to direct analysis of liquids remains uncommon. Previously reported approaches typically rely on confined liquid geometries, such as sealed micro-containers, capillaries, or absorbent supports. Günther et al. [21] deposited liquid samples into Teflon® micro-beakers and sealed them with Parafilm® to prevent evaporation, uncovering the surface by laser-drilling through the film immediately before analysis. Boué-Bigne et al.[22] investigated liquid ablation only in the context of evaluating ablation yields of aqueous standards, where absorption coefficients were modified by chromophore addition. Heilmann et al.[4] analyzed trace elements in organometallic standards and oil samples dissolved in isobutyl methyl ketone and absorbed onto cellulose mounted in a Teflon® holder. More recently, Chbani et al.[23] described the ablation of oil standards contained in silica capillaries, which minimized sample evaporation. In that approach, the capillary was positioned in a holder, a laser-drilled hole provided access to the oil, and carbon concentration was used as an internal standard. While this demonstrates that ablation of oils is feasible and highlights the potential of silica capillaries for handling micro-quantities, the use of carbon as an internal standard remains problematic[24]. Accurate quantification requires knowledge of the carbon content in each sample[23], which is difficult in ICP-MS due to high carbon background from atmospheric CO_2 [25, 26], low sensitivity[25], and additional challenges related to non-spectral interferences[12].

Reliable application of carbon as an internal standard therefore often requires complementary analytical techniques, which compromises analytical simplicity.

Consequently, a simple and robust LA-ICP-MS strategy that enables direct elemental analysis of oils without increased experimental complexity is still lacking. In this work, we address this gap by demonstrating that fast screening elemental analysis of oils can be achieved by direct ablation of microlitre-scale oil droplets deposited onto a flat PTFE substrate. The influence of key ablation parameters is systematically investigated, and indium is evaluated as an internal standard for correcting signal fluctuations and matrix-related effects. The performance of the proposed droplet-based LA-ICP-MS approach is demostrated by analysis of set of engine and lubricating oil samples, with results compared to conventional ICP-MS following acid digestion.

2 Material and methods

2.1 Instrumentation

All experiments were conducted using LA instrument LSX-213 G2+ (Teledyne Photon Machines, Bozeman, USA) coupled to ICP-MS NexIon 5000 (PerkinElmer, Shelton, Connecticut, USA). Evaluation of elemental fractionation was also carried out using… Samples were weighted on balances METTLER AE 200 (METTLER-TOLEDO, Columbus, Ohio, USA). For digestion of the samples prior to conventional ICP-MS analysis, a microwave digestion system SpeedWave 4 (Berghof, Einigen, Germany) was employed.

For homogenization of the samples intended for LA-ICP-MS analysis, a Heidolph multi Reax shaker (Heidolph Scientific Products GmbH, Schwabach, Germany) was used in combination with an ultrasonic bath Elmasonic S30 (Elma Schmidbauer GmbH, Singen, Germany). Centrifugation of the samples was carried out using a Sigma 2-16KL centrifuge (Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany). The solid wear particles were monitored using optical microscope (Student 303, Sagittarius Optical, Czech Republic).

2.2 Samples and reagents

CONOSTAN® S-21 standard containing 21 elements (at 100 mg/kg level) and CONOSTAN® blank (both from SCP Science, Clark Graham, Baie d'Urfe, Canada) were used for preparation of calibration standards at various concentrations and for optimization of the ablation process. Xylene (PENTA s.r.o., Prague, Czech Republic) and indium(III) acetoacetonate (Sigma Aldrich, Steinheim, Germany) was used for preparation of the internal standard (IS) solution.

HNO_3 (67-69%, Analpure® grade, Analytika spol. s.r.o., Prague, Czech Republic) was used for stabilization of elements in solution during the conventional ICP-MS measurement and, together with H_2O_2 (30%, PENTA s.r.o., Prague, Czech Republic), for microwave-assisted acid digestion of samples. For calibration, single element standards of Al, Cr, Ca, Fe, Mg, Ti, V, P, Zn, Mo, B, Ba, Mn, Ni, cu, Cd, Sn and Pb (all 1000±2 mg/L, Astasol®, Analytika spol. s.r.o., Prague, Czech Republic) were used.

Besides that, twenty real samples of engine oils were used for the analysis of real samples.

2.3 Preparation of the calibration standards and samples for LA-ICP-MS

First of all, internal standard solution containing 0.1 % (m/m) In in form of indium(III) acetoacetonate in xylene was prepared. The solution needed to be homogenized in the ultrasonic bath for 30 s to ensure, all the indium(III) acetoacetonate is dissolved.

From CONOSTAN® S-21 standard and CONOSTAN® blank (both from SCP Science, Clark Graham, Baie d'Urfe, Canada), set of calibration standards of different concentrations was prepared (0.05, 0.1, 0.5, 1, 5, 10, 50 and 100 mg/kg). To one gram of each calibration standard, 10 µL od IS xylene solution (made in previous step) was added. Plastic test tubes containing the standards were then centrifuged for 30 seconds at 6000 rpm to collect the viscous oil standard from the tube walls after mixing with the internal standard, shaken for 20 minutes, and centrifuged again. The samples of oils were treated the same way.

Spike recovery experiments were performed using samples No. 10 and 17 (see **Table S4** for the list of samples). Recovery was assessed at two spike levels, 10 and 50 mg/kg. The samples were prepared by mixing the sample with the CONOSTAN® S-21 standard at mass ratios of 9:1 for the 10 mg/kg spike level and 1:1 for the 50 mg/kg spike level. Indium was subsequently added as an internal standard, and the samples were treated in accordance with the procedure described above.

Standards and samples were then transferred into the plastic syringe (Terumo Corporation, Tokyo, Japan), with dosing needle with diameter of 100 µm (HOTAIR®, Ostrava, Czech Republic). The drops were allowed to drip freely from the dosing needle, which ensures the similar volume of all droplets (3–4 µL). Droplets were deposited onto the polytetrafluorethylene (PTFE; Onpira, Czech Republic), substrate, which was determined in our previous work as most suitable material for laser ablation of liquids[27]. For testing different droplet volume, Hamilton® syringe (10 µL, 700Series, Hamilton®, Reno, NV, USA) was used. Deposited droplets on PTFE a substrate was placed into the ablation cell and LA-ICP-MS analysis was performed.

2.4 Sample digestion for ICP-MS measurement

Approximately 0.2 g of each sample was weighed into a digestion tube. Subsequently, 3 mL of HNO_3 and 3 mL of H_2O_2 were added, and the mixture was left to stand for 15 minutes. Microwave-assisted acid digestion was then carried out under the conditions specified in **Table S1**. After digestion, the solutions were diluted to a final volume of 50 mL with Milli-Q water (Millipore, Bedford, USA). Further dilutions were prepared by factors of 10 and 1000 to a total volume of 10 mL. Indium (In) was added as an internal standard. Each sample was prepared in two replicates. CONOSTAN® S-21 standard for evaluation of recovery was treated the same way. ICP-MS analyses were subsequently performed.

2.5 ICP-MS and LA-ICP-MS measurement

The operating conditions for ICP-MS and LA-ICP-MS measurements are summarized in **Table S2**. Calcium, iron, chromium and titanium were analysed using mass shift mode with the dynamic reaction cell (DRC) with ammonia as reaction gas to minimize major spectral interferences, such as Ar^+, ArO^+, ArC^+ and SO^+ respectively. The values obtained by conventional ICP-MS were used as reference values.

For LA-ICP-MS measurements, the ablation cell was initially purged with helium. Various laser ablation parameters were systematically investigated, including laser fluence, laser frequency, the number of laser shots, beam diameter and the volume of the oil droplets.

2.6 Calculation of the limit of detection and limit of quantification for LA-ICP-MS

In the present study, limits of detection (LOD) values were calculated from linear regression analysis of calibration data according to Equation (1)[28]:

$$LOD = \frac{s_{yx}}{b} t_{(1-\alpha;\nu_{eff})} \cdot \sqrt{1 + \frac{1}{n} + \frac{\bar{c}^2}{\sum n(c_i - \bar{c})^2}} \quad (1)$$

where s_{yx} is residual standard deviation, b is the slope of the regression, $t_{(1-\alpha,\, \nu\text{eff})}$ is the critical value of the Student's t-distribution, n is the number of measurements, $\bar{c}$ is the mean concentration, and c_i represents individual standard concentration. Limit of quantitation (LOQ) values were subsequently derived as three times the corresponding LOD values.

2.7 Calculation of recovery and its uncertainties

Spike recovery was calculated using Equation (2):

$$R = \frac{c_i - f c_0}{(1-f) c_{std}} \quad (2)$$

where c_i is the measured concentration of the element and, c_0 is concentration in the unspiked sample, f is mixing factor and c_{std} is concentration of standard used for spiking (CONOSTAN® S-21).

Recovery for real samples and CONOSTAN® S-21 oil standard was calculated using Equation (3):

$$R = \frac{c_i}{c_{ref}} \quad (3)$$

where c_i, is the measured concentration of the element and c_{ref} is reference concentration obtained by conventional ICP-MS measurement.

The uncertainty of recovery (u_R) was calculated using Equation (4):

$$u_R = R \sqrt{\left(\frac{u_i}{c_i}\right)^2 + \left(\frac{u_{ref}}{c_{ref}}\right)^2} \quad (4)$$

where u_i and u_{ref} are the standard uncertainties of measured and reference concentrations, respectively. These uncertainties were expressed as repeatability (sample standard deviation).

3 Results and discussion

3.1 Optimization of laser ablation

Laser ablation of liquid droplets fundamentally differs from ablation of solid samples due to the absence of a rigid surface, which can lead to droplet deformation or partial ejection during irradiation. Therefore, careful balance between ablation efficiency and droplet stability must be established to obtain reproducible analytical signals. For optimization of the ablation process, CONOSTAN S-21 oil standard (element concentrations 100 mg/kg) was used, and signals of five isotopes (^{55}Mn, ^{63}Cu, ^{111}Cd, ^{138}Ba and ^{208}Pb) were monitored. These isotopes were selected to cover a wide mass range. The influence of laser ablation parameters, including the number of laser shots, repetition rate, laser fluence, and droplet volume, was systematically investigated. Each parameter is discussed below, and a summary of the optimized ablation conditions is provided in **Table S2**.

3.1.1 Different number of laser shots and frequency

The effect of the number of laser shots on signal intensity was investigated using 1, 2, 5, 10, 50, 100, and 300 laser shots at a constant laser fluence of 1 J/cm² and repetition rate of 10 Hz. For all monitored isotopes, signal intensity increased with the number of laser shots, reflecting the increasing amount of ablated material. A signal plateau was reached at 50 shots, beyond which no further significant increase in signal intensity was observed (**Fig. 1**)

Subsequently, the effect of laser repetition rate was investigated at 1, 2, 5, 10, 15, and 20 Hz, using 50, 100, and 300 laser shots (**Fig. 2**). In general, signal intensity increased with increasing repetition rate. However, at lower repetition rates (1 and 2 Hz), pronounced signal variability was observed for most elements. This behaviour thus demonstrates the need to use higher frequencies to achieve more stable measurements.

In LA-ICP-MS, transient signals can be processed using averaging, median, or signal integration approaches. Consequently, an appropriate combination of the number of laser shots and repetition rate must provide not only sufficient signal intensity but also a signal duration compatible with reliable data processing. Based on these considerations, 100 laser shots at a repetition rate of 5 Hz were selected as optimal, resulting in a transient signal of approximately 20 s. Alternative parameter combinations, such as 300 laser shots at 10 Hz, produced longer signals of approximately 30 s with comparable stability. However, the selected conditions offer improved time efficiency while minimizing excessive energy input into the droplet, which may result in sample heating or degradation.

3.1.2 Different fluence of the laser

Laser fluence is a key parameter in ablation, influencing both signal intensity and sample integrity. Its influence on signal intensity was systematically investigated by varying fluence from 0.3 to 1.8 J/cm^2 (**Fig. 3A**). Signal intensity increased with laser fluence with the first detectable signal observed at a fluence of 0.3 J/cm^2 (for ^{138}Ba). Above 1.2 J/cm², the signal intensity reached a plateau for all measured isotopes. The fluence of 1.2 J/cm^2 was thus selected as optimal, because visual inspection revealed partial droplet disruption and the formation of secondary microdroplets around the ablation site at higher fluences (**Fig. 3B**). Such effects may increase the risk of samples cross-contamination within the ablation cell.

3.1.3 Different beam diameter

The influence of beam diameter on signal intensity was investigated for both laser systems (193 nm and 213 nm). Beam diametr is a key parameter in laser ablation, as larger diameters generally increase the amount of ablated material and thus signal intensity. However, excessive material removal may lead to inefficient aerosol transport and signal instability, particularly in systems without rapid washout ablation cells.[29, 30]. Such behaviour is well documented in laser ablation mapping of solid samples; however, the dynamics during ablation of liquid droplets may differ due to their distinct physical properties.

For the 213 nm system, beam diameters of 10, 20, 50, 100, and 200 µm were tested. A droplet of the CONOSTAN® S-21 oil standard was ablated at a laser fluence of 1.2 J/cm², a repetition rate of 5 Hz, and 100 laser shots. For the 193 nm system, beam diameters of 10, 20, 35, and 50 µm were evaluated, as larger beam diameters were not available on this instrument. Droplet was measured at fluence of 3.81 J/cm^2. The results are presented in **Fig. 4**.

No measurable signal was observed for any monitored element at beam sizes below 50 µm for the 213 nm system and below 20 µm for the 193 nm system. In contrast, stable and reproducible signals were obtained at beam diameters of 50 µm and above for the 213 nm system, despite the absence of a fast washout ablation cell. For the 193 nm system, reproducible

and stable signals were observed at beam sizes of 20 µm and above. These results indicate that larger beam diameters are required to achieve sufficient and stable signal intensity for liquid sample analysis under the specified experimental conditions. The lower threshold observed for the 193 nm system is consistent with its higher ablation efficiency.

3.1.4 Different droplet volume

Precise and reproducible dosing of very small liquid volumes can be analytically challenging and may affect measurement repeatability. To assess this effect, the influence of droplet volume on signal intensity was investigated using droplets ranging from 0.2 to 10 µL (**Fig. 5A**). The signal intensity of all measured isotopes was slightly higher for small (≥1 µL) droplets, likely due to enhanced droplet heating (**Fig. 5B**). However, within the microlitre range, these effects were less pronounced, and the signal became largely independent of droplet size. At higher volumes, signal variability decreased, indicating improved measurement stability. Therefore, when using droplets of 3–4 µL in our work (see Section 2.3), minor variations in droplet volume during dosing have a negligible impact on analytical accuracy.

In addition to droplet size, method robustness is crucial for practical application, particularly with respect to laser beam focusing, which can be more challenging for liquid samples in comparison to solid, as well as droplet stability during measurement.

Fig. S1 shows that the effect of incorrect focusing becomes significant only at defocusing values exceeding 0.5 mm, providing a sufficiently wide tolerance window to minimize errors associated with improper beam alignment. Furthermore, repeated ablation of the droplet does not affect its geometry or physical properties, as demonstrated in **Fig. S2** Even after 49 ablation cycles, the measurement remains stable, with no substantial impact on analytical precision.

3.1.5 Elemental fractionation

Another critical aspect of LA-ICP-MS analysis is elemental fractionation, which refers to the preferential loss or gain of certain elements or isotopes during laser ablation and subsequent transport to the plasma. Fractionation can lead to inaccurate quantification if not properly accounted for. Since laser ablation of liquids is less common than that of solid samples and liquids exhibit markedly different physical properties, the assessment of fractionation is particularly important in these matrices.[31]

Fractionation was evaluated using the CONOSTAN® S-21 oil standard (100 mg/kg), which was ablated using two laser systems operating at wavelengths of 213 nm and 193 nm. For the 213 nm system, ablation was performed at five different laser fluences (0.5, 1, 2, 3, and 4 J/cm²). For the 193 nm system, eight fluences were tested (2.5, 2.7, 3.0, 3.2, 3.4, 3.6, 3.8, and 4.1 J/cm²). In both cases, indium was employed as an internal standard for signal correction (sample preparation is described in Section 2.3).

Fractionation was assessed by quantifying the measured signals using the certified reference materials NIST SRM 610 (for 193 nm measurements) and NIST SRM 612 (for 213 nm measurements), as these materials exhibit minimal elemental fractionation under typical ablation conditions. Uncertified reference values for these CRMs were taken from[32]. The resulting concentrations were then relativized to evaluate the extent of elemental fractionation.

Measurements with the 213 nm laser were performed at a repetition rate of 20 Hz using 400 laser shots and a spot diameter of 200 µm. Isotopes ^{40}Ca, ^{48}Ti, ^{52}Cr, and ^{56}Fe were measured in reaction cell mode, as described in Section 2.5. Measurements with the 193 nm laser were

conducted under Dosage 8, SPR =500 ms, Rep rate 20 Hz.Representative results for the 193 nm system at 3.8 J/cm² and for the 213 nm system at 2.0 J/cm² are shown in **Fig. 6**. These fluences were selected as representative conditions because fractionation did not vary substantially across the tested fluence range for the 213 nm system and showed minimal variation between 3.0 and 4.1 J/cm² for the 193 nm system. Detailed fractionation data for all tested fluences are provided in **Table S3**.

As shown in **Fig. 6**, fractionation factors ranged from 0.84 to 1.22 for the 193 nm system and from 0.77 to 1.16 for the 213 nm system at the selected fluences. Boron exhibited a notably lower fractionation factor (0.56 for the 213 nm system). This behaviour is consistent with its higher volatility and potential plasma-induced discrimination in ICP-MS systems, which may explain its systematic underestimation. A pronounced difference between the two systems was observed for phosphorus: fractionation was relatively low for the 213 nm system (0.66) but significantly higher for the 193 nm system (1.98). Significant differences were also observed for barium and calcium; however, this may be partially attributed to the use of different monitored isotopes for each laser system.

Overall, most elements did not exhibit substantial fractionation in either system. These results support the suitability of LA-ICP-MS for the elemental analysis of oil matrices under the tested experimental conditions.

3.2 Limit of quantification for selected elements for LA-ICP-MS

LOQ is critical performance parameter for evaluating the applicability of LA-ICP-MS to direct oil analysis. A comparison of LOQ values obtained by LA-ICP-MS with and without internal standardization (IS) is summarized in **Table 1**. For the majority of investigated elements, the application of indium as an internal standard resulted in lower LOQ values, demonstrating its effectiveness in compensating for signal fluctuations.

The only exception is calcium, for which the LOQ without IS is slightly lower; however, as calcium is typically present in engine oils at high concentrations, this difference has no practical impact on routine oil analysis The LOQs obtained in this study with IS are comparable to those reported by Chbani et al.[23], and are approximately an order of magnitude higher than those reported by Heilmann et al.[4], whose data were evaluated using the isotope dilution method, known to significantly reduce detection limits[33].

Notably, the LOQs for ^{63}Cu are higher than those of the other analysed elements, likely due to the naturally elevated background signal of the copper. Overall, the obtained LOQ values confirm that droplet-based LA-ICP-MS is primarily suited for the determination of elements present at >mg/kg concentration levels in oils. While the method does not compete with digestion-based ICP-MS for ultra-trace elemental analysis, the use of internal standardization is an effective approach to improve analytical performance.

Table 1 – Comparison of LOQ values for LA-ICP-MS with and without IS for selected isotopes. LOQ values are expressed in mg/kg.

	$^{52/86}$Cr	$^{40/57}$Ca	$^{56/90}$Fe	$^{48/131}$Ti	^{27}Al	^{24}Mg	^{51}V	^{31}P	^{66}Zn
with IS	1.7	8.1	2.0	1.5	2.9	1.3	0.7	7.5	0.9
without IS	2.3	6.5	2.3	2.2	4.1	2.9	2.3	8.4	2.6
	^{98}Mo	^{11}B	^{138}Ba	^{55}Mn	^{60}Ni	^{63}Cu	^{111}Cd	^{118}Sn	^{208}Pb
with IS	0.8	2.8	0.6	3.5	1.0	14	1.5	0.7	0.9
without IS	2.1	3.8	2.6	4.1	2.5	16	3.2	2.6	3.8

3.3 Method validation

3.3.1 Conventional ICP-MS

To verify that conventional ICP-MS provides accurate results suitable for use it as reference values, the CONOSTAN® S-21 standard was analysed and spike recoveries were evaluated. The results are presented in **Table 2**. For most elements, the obtained recoveries range from 86.4–105.6%, with the exception of B. The low recovery of B (60.7 %) demonstrates that its accurate determination by conventional ICP-MS is not feasible under the present conditions, primarily due to boron's volatility and memory effects, which lead to signal bias and reduced apparent recoveries.

Table 2 – Recoveries of elements in CONOSTAN® S-21 oil standard (100 mg/kg) for conventional ICP-MS with corresponding standard uncertainties (k = 1, in the brackets).

	$^{52/86}$Cr	$^{40/57}$Ca	$^{56/90}$Fe	$^{48/131}$Ti	^{27}Al	^{24}Mg	^{51}V	^{31}P	^{66}Zn
ICP-MS	95.3 (1.2)	89.3 (7.7)	92.2 (0.6)	93.5 (0.8)	100.2 (0.3)	104.8 (0.2)	98.5 (0.6)	101.6 (0.8)	100.7 (0.6)
	^{98}Mo	^{11}B	^{138}Ba	^{55}Mn	^{60}Ni	^{63}Cu	^{111}Cd	^{118}Sn	^{208}Pb
ICP-MS	100.2 (0.7)	60.7 (0.7)	86.4 (0.3)	95.6 (0.7)	105.6 (0.2)	100.7 (0.1)	101.6 (0.2)	91.8 (3.5)	101.1 (4.5)

3.3.2 LA-ICP-MS spike recovery

To evaluate the accuracy of the method, spike recovery experiments were performed at two concentration levels using two oil samples. The data were processed both with internal standardization, using indium (In) as the internal standard, and without internal standardization. Results obtained are presented in **Table 3**. The oil samples (10 and 17) were selected based on their elemental composition to ensure that all investigated elements were adequately represented.

The results clearly demonstrate that data processed using internal standardization exhibit higher and more consistent recoveries than those obtained without internal standardization. When internal standardization was applied, accuracy was significantly better at the higher spike level, with all values of recoveries falling within the range of 85–138 %. The elevated recovery observed for Cu in sample 10 may be attributed to the fact that this spike level is close to the limit of quantification (LOQ). The reason for the higher recovery of Ni at

the lower spike level remains unclear; however, it may be related to a significantly different ablation rate of sample 10 compared to the standard. This interpretation is supported by the results obtained for sample 17, where recoveries for both mentioned elements fall within the range of 93–99 %.

In contrast, recoveries obtained without internal standardization are considerably lower, ranging from 39–104 %. For sample 17 at the higher spike level (50 mg/kg), recoveries between 82–104% were achieved, which can be considered acceptable. At the lower spike level (10 mg/kg), however, the proportion of the original sample matrix is substantially higher (approximately 9:1 sample to spike) compared to the 1:1 ratio at 50 mg/kg. As a result, matrix-related effects differing from those of the calibration standard become more pronounced, leading to greater deviations in recovery. These findings indicate that the observed differences are primarily driven by matrix effects. Internal standardization effectively compensates for these matrix-induced variations and improves the accuracy and reliability of the LA-ICP-MS analysis of oils.

Overall, these results clearly illustrate the importance of internal standardization in LA-ICP-MS analysis of oils, as the ablation rates can vary significantly between samples.

Table 3 – Spike recovery (%) at two different spike levels (10 and 50 mg/kg) for the two selected samples, with their uncertainty (k = 1, in the brackets). The (–) symbols means, that base element concentration in the sample was significantly higher than the spike level.

IS	Sample No.	Spike level (mg/kg)	$^{52/86}$Cr	$^{40/57}$Ca	$^{56/90}$Fe	$^{48/131}$Ti	^{27}Al	^{24}Mg	^{51}V	^{31}P	^{66}Zn	^{98}Mo	^{11}B	^{138}Ba	^{55}Mn	^{60}Ni	^{63}Cu	^{111}Cd	^{118}Sn	^{208}Pb
Yes	10	10	132 (6)	–	121 (6)	126 (5)	100 (9)	104 (5)	125 (7)	–	–	130 (5)	126 (9)	120 (5)	108 (9)	162 (5)	192 (10)	98 (7)	124 (7)	114 (6)
		50	107 (3)	–	104 (1)	108 (3)	101 (6)	93 (7)	106 (6)	–	–	109 (4)	114 (5)	99 (3)	104 (9)	138 (13)	136 (4)	110 (6)	106 (1)	108 (5)
	17	10	95 (9)	88 (5)	103 (1)	101 (1)	101 (8)	91 (4)	97 (1)	139 (20)	83 (4)	98 (3)	116 (3)	89 (2)	97 (13)	97 (1)	99 (2)	107 (3)	96 (4)	92 (2)
		50	97 (3)	85 (13)	96 (1)	97 (1)	93 (1)	94 (2)	93 (2)	123 (5)	99 (4)	95 (3)	100 (4)	85 (2)	92 (2)	94 (1)	93 (1)	98 (2)	90 (1)	87 (2)
No	10	10	41 (4)	–	39 (4)	40 (3)	47 (4)	43 (1)	47 (4)	–	–	47 (4)	52 (2)	45 (3)	37 (1)	60 (2)	66 (3)	20 (5)	46 (5)	44 (2)
		50	53 (3)	–	53 (3)	54 (4)	51 (3)	53 (4)	52 (4)	–	–	54 (4)	60 (4)	48 (4)	47 (4)	67 (4)	65 (5)	50 (3)	52 (4)	51 (4)
	17	10	46 (4)	43 (8)	49 (2)	47 (3)	79 (7)	78 (8)	75 (7)	89 (8)	86 (9)	77 (8)	87 (8)	70 (7)	62 (11)	80 (8)	75 (8)	82 (7)	75 (7)	71 (8)
		50	92 (4)	82 (5)	90 (4)	90 (4)	86 (2)	88 (3)	86 (3)	104 (5)	91 (4)	87 (3)	95 (5)	82 (4)	85 (3)	87 (2)	84 (2)	87 (3)	83 (2)	83 (3)

3.4 Measurement of real samples (comparison of the methods)

To evaluate the analytical performance of the proposed droplet-based LA-ICP-MS approach, twenty real oil samples of different types (**Table S4**) were analysed, and the obtained results were compared with reference concentrations determined by conventional ICP-MS following microwave-assisted acid digestion. The digestion-based ICP-MS data were used as reference values, as this approach ensures complete decomposition of the organic matrix and homogeneous analyte distribution. The same samples were then analysed by LA-ICP-MS, and the resulting contents were evaluated both with and without IS. Indium was chosen as internal standard, as this element is often used as internal standard in lot of ICP-MS applications[34] and it is not commonly present in oils at significant concentrations. A summary of recoveries obtained for selected elements by LA-ICP-MS with and without internal standardization is provided in **Table 4**, while the corresponding element concentrations determined by conventional ICP-MS are listed in **Table S5**. Overall, the application of internal standardization resulted in improved agreement with reference values and reduced signal variability across the analysed sample set.

When indium was used as internal standard, recoveries for most elements ranged between 74 and 144 %, whereas significantly larger deviations and higher uncertainties were observed without internal standardization. Elements present at higher concentration levels, particularly additive-derived elements such as Ca, Zn, P and Mg, as well as wear-related metals Fe and Al, were quantified with satisfactory accuracy in the majority of samples. For these elements, recoveries with internal standardization typically fell within the 80–120 % interval.

In contrast, recoveries outside the optimal range were predominantly observed for elements present at low concentrations, typically close to the respective limits of quantification. Low recoveries were also reported by Chbani et al.[23], where recoveries were 60 % for V and Pb in concentration of 0.1 mg/kg. Compared to measurements performed without internal standardization, the use of indium significantly reduced both systematic bias and random variability. Without internal standardization, recoveries were frequently below 60 % and relative uncertainties often exceeded 10–20 %, particularly for elements present at low concentrations. This clearly demonstrates that internal standardization is essential for obtaining reliable quantitative data in droplet-based LA-ICP-MS.

From a practical perspective, the obtained results show that the proposed methodology is particularly well suited for routine screening and quality-oriented analysis of oils. The analysis of the samples revealed an excellent correlation between P and Zn, clearly demonstrating the method's capability to reliably quantify additive-related elements. This is particularly evident for additives such as zinc dialkyldithiophosphates (ZDDPs)[35, 36], as well as for elevated concentrations of Ca, B, and Mo associated with additives including calcium sulfonates[35], molybdenum dithiocarbamates[36], and boron-containing compounds[37].

In contrast, for ultra-trace elements present at very low levels, conventional digestion-based ICP-MS remains the method of choice. The droplet-based LA-ICP-MS approach should therefore be regarded as a complementary technique that prioritizes experimental simplicity, rapid analysis and minimal sample preparation over ultimate detection limits.

3.5 Fresh and used engine oil

The ability to quantify wear-related metals directly in used oils is of particular relevance for engine operating condition monitoring and tribological studies, where rapid assessment of lubricant condition and component wear is required. This study also represents a proof-of-concept for determining the elemental composition of solid particles in oils.

Samples 19 and 20 represent fresh and used oil collected from a lawn mower. As shown in **Table S5**, the used oil exhibits higher concentrations of Al and Fe compared to the fresh oil. This increase can be attributed to the transfer of these elements into the lubricant during engine

operation as a result of mechanical wear processes. More importantly, these elements are introduced in the form of wear debris[38, 39] – microscopic solid particles generated by mechanical wear (**Fig. 7**). The presence of such particles poses a potential challenge for direct analytical techniques. This dimension is negligible compared to the applied laser beam diameter of 200 µm used for droplet ablation. Consequently, each laser pulse interacts simultaneously with many particles rather than with individual isolated particles.

Under these conditions, the ablated material can be regarded as spatially- and mass-representative with respect to the particulate fraction present in the droplet. This substantially reduces the risk of particle-related signal fluctuations that may otherwise arise from stochastic sampling of individual wear particles.

As demonstrated by the recovery data summarized in Table 5, the application of indium as an internal standard enabled accurate quantification of aluminium and iron in the used oil sample despite their presence in particulate form. This indicates that internal standardization effectively compensates for variations in ablated mass and transport efficiency associated with heterogeneous droplet composition. Importantly, no additional sample pretreatment or homogenization steps were required prior to LA-ICP-MS analysis. The combination of microlitre-scale droplet ablation and internal standardization thus provides also a practical approach for the analysis of both fresh and used oils containing wear-related particulate matter.

Table 4 – Comparisson of recoveries (%) of selected elements with standard uncertainities (k = 1, in the brackets) for real samples for LA-ICP-MS with and without internal standardization. Values obtained by conventional ICP-MS were chosen as reference values. The (-) symbols means, that measured values were below the detection limit.

No.	LA-ICP-MS	Ca	Fe	Al	Mg	P	Zn	Mo	B
1	with IS	89 (10)	-	-	95 (6)	91 (4)	100 (9)	111 (6)	122 (5)
	without IS	86 (11)	-	-	84 (8)	75 (5)	82 (10)	83 (16)	114 (10)
2	with IS	102 (5)	79 (5)	-	95 (9)	84 (7)	95 (4)	87 (3)	109 (26)
	without IS	88 (13)	96 (13)	-	77 (13)	73 (10)	65 (16)	73 (11)	92 (26)
3	with IS	95 (5)	-	-	82 (7)	89 (6)	102 (6)	112 (11)	124 (5)
	without IS	91 (10)	-	-	94 (9)	86 (9)	82 (18)	113 (13)	126 (12)
4	with IS	92 (4)	-	-	55 (5)	88 (6)	96 (6)	-	112 (3)
	without IS	87 (9)	-	-	56 (7)	74 (10)	67 (16)	-	99 (14)
5	with IS	96 (4)	81 (3)	-	98 (10)	86 (8)	93 (6)	116 (7)	83 (19)
	without IS	67 (13)	90 (13)	-	63 (13)	54 (10)	51 (14)	79 (16)	56 (17)
6	with IS	116 (7)	74 (6)	-	79 (17)	103 (6)	107 (8)	-	137 (8)
	without IS	84 (9)	94 (10)	-	81 (18)	69 (4)	77 (6)	-	119 (9)
7	with IS	109 (6)	101 (3)	-	105 (17)	102 (9)	94 (6)	-	94 (15)
	without IS	98 (13)	105 (11)	-	110 (11)	82 (11)	92 (12)	-	97 (20)
8	with IS	130 (15)	-	-	136 (7)	126 (6)	137 (12)	156 (11)	123 (11)
	without IS	97 (15)	-	-	110 (12)	79 (6)	95 (11)	116 (18)	96 (11)
9	with IS	119 (11)	90 (34)	84 (31)	97 (8)	105 (3)	90 (3)	131 (14)	119 (14)
	without IS	57 (9)	-	-	52 (4)	48 (4)	48 (8)	72 (8)	55 (11)
10	with IS	144 (17)	-	67 (38)	124 (19)	115 (11)	86 (5)	29 (4)	58 (10)
	without IS	42 (6)	-	-	37 (7)	25 (5)	19 (5)	-	-
11	with IS	99 (7)	-	-	96 (7)	98 (6)	91 (5)	106 (4)	120 (7)
	without IS	76 (9)	-	-	87 (10)	82 (9)	93 (10)	101 (13)	146 (27)
12	with IS	102 (8)	-	-	77 (7)	110 (3)	100 (4)	-	160 (12)
	without IS	92 (12)	-	-	72 (9)	71 (4)	87 (8)	-	137 (14)
13	with IS	90 (5)	-	-	91 (7)	82 (2)	96 (4)	-	97 (6)
	without IS	98 (17)	88 (24)	-	80 (19)	73 (9)	98 (13)	-	81 (19)
14	with IS	89 (3)	-	-	75 (15)	83 (3)	91 (8)	123 (13)	121 (11)
	without IS	86 (12)	-	-	82 (17)	79 (5)	92 (11)	126 (16)	143 (25)
15	with IS	-	-	-	-	113 (16)	-	-	-
	without IS	-	-	-	-	88 (14)	-	-	-
16	with IS	-	-	-	-	75 (11)	74 (16)	-	-
	without IS	-	-	-	-	39 (11)	46 (21)	-	-
17	with IS	95 (55)	-	-	-	-	80 (31)	-	-
	without IS	-	-	-	-	-	-	-	-
18	with IS	119 (9)	-	-	-	114 (5)	121 (33)	-	-
	without IS	34 (3)	-	-	-	30 (2)	32 (10)	-	-
19	with IS	129 (8)	-	-	107 (20)	112 (4)	100 (2)	180 (22)	189 (13)
	without IS	66 (6)	-	-	58 (11)	53 (2)	48 (2)	-	105 (12)
20	with IS	129 (11)	104 (9)	86 (7)	106 (19)	111 (3)	102 (5)	157 (15)	168 (4)
	without IS	59 (8)	51 (8)	40 (5)	51 (10)	47 (2)	45 (3)	68 (9)	74 (3)

4 Conclusion

This work demonstrates that LA-ICP-MS can be applied for the direct elemental analysis of oils by simple ablation of microlitre-scale droplets deposited on a flat PTFE substrate. The proposed approach eliminates the need for digestion, dilution, or complex liquid-handling systems, thereby significantly reducing experimental complexity and analysis time.

Systematic optimization of laser parameters confirmed that stable and reproducible signals can be obtained despite the inherently dynamic nature of liquid droplet ablation. The use of indium as an internal standard proved essential for compensating signal fluctuations and matrix-related effects, leading to improved accuracy.

Application to a diverse set of real engine and lubricating oils showed that the method is particularly well suited for the determination of additive-derived elements and wear-related metals, including elements occurring in particulate form in used oils. Nevertheless, conventional digestion-based ICP-MS remains the method of choice for ultra-trace elements levels close to the limits of quantification.

Overall, the droplet-based LA-ICP-MS strategy should be regarded as a complementary analytical tool that prioritizes speed, simplicity, and minimal sample preparation. Its main strength lies in rapid screening, comparative analysis, and process-oriented studies of oils, where direct analysis and reduced experimental overhead provide clear advantages over traditional methodologies.

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CRediT authorship contribution statement

Petr Rudolf: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft**. Martin Šala:** Investigation, Formal analysis, Data curation, Writing – review & editing. **Antonín Kaňa:** Conceptualization, Methodology, Writing – review & editing, Supervision

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] J. Basiron, M.F.B. Abdollah, M.I.C. Abdullah, H. Amiruddin, Lubricant mechanisms of eco-friendly lubricant blended with mineral oil for steel-steel contact, Tribol. Int. 186 (2023) 108653. https://doi.org/10.1016/j.triboint.2023.108653.

[2] J. Liu, M. Ronk, K. Fujimori, H. Lee, Y. Nashed-Samuel, Analysis of Silicone Oil in Prefilled Syringes and Biopharmaceutical Drug Products Using High-Performance Liquid Chromatography, AAPS PharmSciTech 22(2) (2021) 75. https://doi.org/10.1208/s12249-021-01947-6.

[3] J.S.F. Pereira, D.P. Moraes, F.G. Antes, L.O. Diehl, M.F.P. Santos, R.C.L. Guimarães, T.C.O. Fonseca, V.L. Dressler, É.M.M. Flores, Determination of metals and metalloids in light and heavy crude oil by ICP-MS after digestion by microwave-induced combustion, Microchem. J. 96(1) (2010) 4-11. https://doi.org/10.1016/j.microc.2009.12.016.

[4] J. Heilmann, S.F. Boulyga, K.G. Heumann, Development of an isotope dilution laser ablation ICP-MS method for multi-element determination in crude and fuel oil samples, J. Anal. At. Spectrom. 24(4) (2009) 385-390. https://doi.org/10.1039/B819879A.

[5] O.P. Sondhiya, A.K. Gupta, Wear debris analysis of automotive engine lubricating oil using by ferrography, Int. J. Eng. Innov. Technol. 2(5) (2012) 46-54.

[6] S.R. Khan, B. Sharma, P.A. Chawla, R. Bhatia, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES): a Powerful Analytical Technique for Elemental Analysis, Food Anal. Methods. 15(3) (2022) 666-688. https://doi.org/10.1007/s12161-021-02148-4.

[7] L. Poirier, J. Nelson, D. Leong, L. Berhane, P. Hajdu, F. Lopez-Linares, Application of ICP-MS and ICP-OES on the Determination of Nickel, Vanadium, Iron, and Calcium in Petroleum Crude Oils via Direct Dilution, Energy Fuels 30(5) (2016) 3783-3790. https://doi.org/10.1021/acs.energyfuels.5b02997.

[8] S. Martínez, R. Sánchez, J. Lefevre, J.-L. Todolí, Multielemental analysis of vegetable oils and fats by means of ICP-OES following a dilution and shot methodology, J. Anal. At. Spectrom. 35(9) (2020) 1897-1909. https://doi.org/10.1039/D0JA00112K.

[9] P. de Azevedo Mello, J.S. Fagundes Pereira, D.P. de Moraes, V.L. Dressler, É.M. de Moraes Flores, G. Knapp, Nickel, vanadium and sulfur determination by inductively coupled plasma optical emission spectrometry in crude oil distillation residues after microwave-induced combustion, J. Anal. At. Spectrom. 24(7) (2009) 911-916. https://doi.org/10.1039/B904194J.

[10] R.S. Amais, C.D.B. Amaral, L.L. Fialho, D. Schiavo, J.A. Nóbrega, Determination of P, S and Si in biodiesel, diesel and lubricating oil using ICP-MS/MS, Anal. Methods 6(13) (2014) 4516-4520. https://doi.org/10.1039/C4AY00279B.

[11] C. Walkner, R. Gratzer, T. Meisel, S.N.H. Bokhari, Multi-element analysis of crude oils using ICP-QQQ-MS, Org. Geochem. 103 (2017) 22-30. https://doi.org/10.1016/j.orggeochem.2016.10.009.

[12] L.N. Viana, T.D. Saint'Pierre, Direct determination of Cr and Ni in oil samples by isotope dilution and external standard calibration using inductively coupled plasma mass spectrometry, Microchem. J. 151 (2019) 104219. https://doi.org/10.1016/j.microc.2019.104219.

[13] C. Lienemann, S. Dreyfus, C. Pecheyran, O.F.X. Donard, Trace metal analysis in petroleum products: sample introduction evaluation in ICP-OES and comparison with an ICP-MS approach, Oil gas sci. technol. 62(1) (2007) 69-77. https://doi.org/10.2516/ogst:2007006.

[14] M.A. Gab-Allah, G.E. S., S.A. B., H. and Gamal, Critical Review on the Analytical Methods for the Determination of Sulfur and Trace Elements in Crude Oil, Crit. Rev. Anal. Chem. 50(2) (2020) 161-178. https://doi.org/10.1080/10408347.2019.1599278.

[15] E. Björn, W. Frech, Introduction of high carbon content solvents into inductively coupled plasma mass spectrometry by a direct injection high efficiency nebuliser, Anal. Bioanal. Chem. 376(2) (2003) 274-278. https://doi.org/10.1007/s00216-003-1874-5.

[16] S.L. dos Anjos, J.C. Alves, S.A. Rocha Soares, R.G.O. Araujo, O.M.C. de Oliveira, A.F.S. Queiroz, S.L.C. Ferreira, Multivariate optimization of a procedure employing microwave-assisted digestion for the determination of nickel and vanadium in crude oil by ICP OES, Talanta 178 (2018) 842-846. https://doi.org/10.1016/j.talanta.2017.10.010.
[17] F. Tokay, S. Bağdat, Determination of Iron and Copper in Edible Oils by Flame Atomic Absorption Spectrometry After Liquid–Liquid Extraction, J. Am. Oil Chem. Soc. 92(3) (2015) 317-322. https://doi.org/10.1007/s11746-015-2603-x.
[18] V. Fernández-Pérez, M.M. Jiménez-Carmona, M.D. Luque de Castro, Continuous liquid–liquid extraction using modified subcritical water for the demetalisation of used industrial oils, Anal. Chim. Acta 433(1) (2001) 47-52. https://doi.org/10.1016/S0003-2670(01)00779-6.
[19] Z. Kowalewska, B. Izgi, S. Saracoglu, S. Gucer, Application of liquid-liquid extraction and adsorption on activated carbon to the determination of different forms of metals present in edible oils, Chem. Anal. (Warsaw) 50(6) (2005) 1007.
[20] G.M.J. Al Kaisy, M.I. Abdul Mutalib, M.A. Bustam, J.-M. Leveque, N. Muhammad, Liquid-Liquid extraction of aromatics and sulfur compounds from base oil using ionic liquids, J. Environ. Chem. Eng. 4(4, Part A) (2016) 4786-4793. https://doi.org/10.1016/j.jece.2016.11.011.
[21] D. Günther, R. Frischknecht, H.-J. Müschenborn, C.A. Heinrich, Direct liquid ablation: a new calibration strategy for laser ablation-ICP-MS microanalysis of solids and liquids, Fresenius J. Anal. Chem. 359 (1997) 390-393.
[22] F. Boué-Bigne, B. J. Masters, J. S. Crighton, B. L. Sharp, A calibration strategy for LA-ICP-MS analysis employing aqueous standards having modified absorption coefficients, J. Anal. At. Spectrom. 14(11) (1999) 1665-1672. https://doi.org/10.1039/A905479K.
[23] M. Chbani, M.-C. Boiron, C. Peiffert, J. Marin, C. Lorgeoux, R. Michels, Quantitative Measurement of Multiple Elements in Micro-Quantities of Crude Oil Using In Situ Analysis by Laser Ablation-ICP-MS, Geost. Geoanal. Res. 48(4) (2024) 823-835. https://doi.org/10.1111/ggr.12580.
[24] D.A. Frick, D. Günther, Fundamental studies on the ablation behaviour of carbon in LA-ICP-MS with respect to the suitability as internal standard, J. Anal. At. Spectrom. 27(8) (2012) 1294-1303. https://doi.org/10.1039/C2JA30072A.
[25] F. Laborda, C. Trujillo, R. Lobinski, Analysis of microplastics in consumer products by single particle-inductively coupled plasma mass spectrometry using the carbon-13 isotope, Talanta 221 (2021) 121486. https://doi.org/10.1016/j.talanta.2020.121486.
[26] T. Vonderach, A. Gundlach-Graham, D. Günther, Determination of carbon in microplastics and single cells by total consumption microdroplet ICP-TOFMS, Anal. Bioanal. Chem. 416(11) (2024) 2773-2781. https://doi.org/10.1007/s00216-023-05064-0.
[27] P. Rudolf, K. Lapčíková, A. Randová, A. Kaňa, Evaporation dynamics of sessile droplets in the ablation cell for LA-ICP-MS analysis of liquids, Anal. Chim. Acta 1359 (2025). https://doi.org/10.1016/j.aca.2025.344127.
[28] L.A. Currie, Nomenclature in evaluation of analytical methods including detection and quantification capabilities: (IUPAC Recommendations 1995), Anal. Chim. Acta 391(2) (1999) 105-126. https://doi.org/10.1016/S0003-2670(99)00104-X.
[29] C. Neff, P. Becker, D. Günther, Parallel flow ablation cell for short signal duration in LA-ICP-TOFMS element imaging, J. Anal. At. Spectrom. 37(3) (2022) 677-683. https://doi.org/10.1039/D1JA00421B.
[30] P. Becker, J. Koch, D. Günther, Impact of ablation cell design in LA-ICP-MS quantification, J. Anal. At. Spectrom. 37(9) (2022) 1846-1854. https://doi.org/10.1039/D2JA00167E.

[31] D. Käser, T. Van Acker, J. Koch, B. Hattendorf, D. Günther, Evaluation of laser-induced and ICP-induced elemental fractionation using laser ablation-ICP-TOFMS, J. Anal. At. Spectrom. 40(9) (2025) 2408-2417. https://doi.org/10.1039/D5JA00173K.
[32] N.J.G. Pearce, W.T. Perkins, J.A. Westgate, M.P. Gorton, S.E. Jackson, C.R. Neal, S.P. Chenery, A Compilation of New and Published Major and Trace Element Data for NIST SRM 610 and NIST SRM 612 Glass Reference Materials, Geostandards Newsl. 21(1) (1997) 115-144. https://doi.org/10.1111/j.1751-908X.1997.tb00538.x.
[33] L.L. Yu, J.D. Fassett, W.F. Guthrie, Detection Limit of Isotope Dilution Mass Spectrometry, Anal. Chem. 74(15) (2002) 3887-3891. https://doi.org/10.1021/ac011254l.
[34] S.C. Wilschefski, M.R. Baxter, Inductively Coupled Plasma Mass Spectrometry: Introduction to Analytical Aspects, Clin Biochem Rev 40(3) (2019) 115-133. https://doi.org/10.33176/aacb-19-00024.
[35] L. Ramopoulou, L. Widder, J. Brenner, A. Ristic, G. Allmaier, Atmospheric pressure matrix-assisted laser desorption/ionization mass spectrometry of engine oil additive components, Rapid Commun. Mass Spectrom. 36(9) (2022) e9271. https://doi.org/10.1002/rcm.9271.
[36] A. Thornley, Y. Wang, C. Wang, J. Chen, H. Huang, H. Liu, A. Neville, A. Morina, Optimizing the Mo concentration in low viscosity fully formulated oils, Tribol. Int. 168 (2022) 107437. https://doi.org/10.1016/j.triboint.2022.107437.
[37] Ö. Karataş, T. Yüksel, Experimental investigation of the effects of boron oil additive in internal combustion engine, Fuel 353 (2023) 129234. https://doi.org/10.1016/j.fuel.2023.129234.
[38] S. Yang, N. Cao, B. Yu, Wear debris measurement in lubricating oil based on inductive method: A review, Meas. Control. 56(7-8) (2023) 1422-1435. https://doi.org/10.1177/00202940231159117.
[39] Y. Iwai, T. Honda, T. Miyajima, S. Yoshinaga, M. Higashi, Y. Fuwa, Quantitative estimation of wear amounts by real time measurement of wear debris in lubricating oil, Tribol. Int. 43(1) (2010) 388-394. https://doi.org/10.1016/j.triboint.2009.06.019.