On the performance of laser-induced breakdown spectroscopy for direct determination of trace metals in lubricating oils ☆

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) provides a technique to directly determine metals in viscous liquids and especially in lubricating oils. A specific laser ablation configuration of a thin layer of oil applied on the surface of a pure aluminum target was used to evaluate the analytical figures of merit of LIBS for elemental analysis of lubricating oils. Among the analyzed oils, there were a certified 75cSt blank mineral oil, 8 virgin lubricating oils (synthetic, semi-synthetic, or mineral and of 2 different manufacturers), 5 used oils (corresponding to 5 among the 8 virgin oils), and a cooking oil. The certified blank oil and 4 virgin lubricating oils were spiked with metallo-organic standards to obtain laboratory reference samples with different oil matrix. We first established calibration curves for 3 elements, Fe, Cr, Ni, with the 5 sets of laboratory reference samples in order to evaluate the matrix effect by the comparison among the different oils. Our results show that generalized calibration curves can be built for the 3 analyzed elements by merging the measured line intensities of the 5 sets of spiked oil samples. Such merged calibration curves with good correlation of the merged data are only possible if no significant matrix effect affects the measurements of the different oils. In the second step, we spiked the remaining 4 virgin oils and the cooking oils with Fe, Cr and Ni. The accuracy and the precision of the concentration determination in these prepared oils were then evaluated using the generalized calibration curves. The concentrations of metallic elements in the 5 used lubricating oils were finally determined.

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1. Introduction

Quantitative analysis of trace metals in engine lubricating oils is required for industrial applications. As additives, metallo-organic compounds are incorporated into lubricating oils to improve lubricating capacity and obtain specific properties such as antioxidant, anticorrosive, dispersing or antiwear [1]. Such compounds involve a large number of elements, for example Mg, Si, Ca, Zn and Ba [1,2]. Precise control of the amount of metals in lubricant production guarantees therefore the targeted performances. On the other hand, metals such as Fe, Al, Cr or Ni, can be introduced into lubricating oil by contamination or by wears in an engine during its operation. Physical wear can be due to friction between the different parts of the engine, high temperature or pressure imposed to the oil during the use, which leads to the generation of debris of metals in the oil. Corrosion leads to chemical wear. The results are either soluble metallo-organic compounds or metallic debris of different sizes. A part of the metallic debris of small size produced due to either physical or chemical wear is not retained by collectors or filters. They remain suspended in the circulating oil and are transported to the different locations of the engine. The sizes of such debris can be much smaller than a few micrometers [3]. Therefore the monitoring and the determination of the metal content in lubricating oils, which may come from either metallo-organic compounds or nanometric metal debris, would provide an efficient way to alert and diagnose any defective functioning in oil-lubricated engines, and if possible before the failures occur [4]. The complexity of the matrix, the high viscosity and the high organic loads however represent serious challenges for analytical chemistry to deal with lubricating oils.

In general, indirect analysis procedures involving an elaborated sample preparation are considered as established techniques for the determination of metals in oils. Such sample preparation methods can include wet digestion, combustion, dilution, emulsification, extraction, etc. [5]. The associated analytical techniques are often atomic absorption spectrometry (AAS) [6–10], and inductively coupled plasma optical emission spectrometry (ICP–OES) [11] or mass spectrometry (ICP–MS)

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[12]. Good analytical performance can be obtained with a limit of detection (LoD) in the range of ng/g (ppb in weight) for a dilution factor of the initial oil of typically from 10 to 100 [2]. The above established indirect analytical methods exhibit however disadvantages not only because of the highly complex and expensive equipment, but also because of the required expertise and long time for reliable sample preparation. This increases the cost of the analysis and prevents in situ or online monitoring and measurement. Direct determination of metal content in oil is therefore required to satisfy the need of quick analysis. X-ray fluorescence spectrometry (XRF) has been demonstrated as a suitable technique for direct determination of metals in lubricating oils [13]. LoD in the order of μg/g (ppm in weight) can be obtained with a typical integration time of 100 s.

Laser-induced breakdown spectroscopy (LIBS) provides an alternative technique for direct and rapid determination of metals in lubricating oils [14–16]. The application of LIBS to oil analysis suffers however from the low laser ablation efficiency of liquids, leading to higher instability and lower temperature of the plasma generated on a liquid surface than that generated on a solid surface [17]. Our recent works demonstrated a specific oil ablation configuration where a thin (~15 μm) film of oil is coated on the polished surface of a pure metallic (aluminum for instance) target. An incident laser pulse produces a hot metallic plasma which in turn, through its interaction with the oil film, induces the breakdown of the coating layer. A mixture plasma containing evaporated species from the target and those from the oil layer can be observed about 1 μs after the initiation of the aluminum plasma with a high temperature in the range around 15,000 K [18]. Such high temperature allows efficient excitation of the species contained in the oil layer, metallic as well as nonmetallic elements such as Cl with high excitation energy. The use of this specific oil ablation configuration for metallic elements determination has then been investigated. Limits of detection ranging from several ppm to hundreds ppb have been demonstrated for various metals [19]. These LoDs are close to those reachable with XRF and approaching the performances of the indirect oil analysis techniques such as AAS and ICP–OES.

In this paper we report on an extensive investigation on the figures of merit of LIBS for direct determination of metals in lubricating oils. The above mentioned ablation configuration of thin oil layer is used since it provides the best LoDs of metal determination in viscous liquids with LIBS [19]. A critical point is whether, with a given metallic substrate and in the same controllable experimental conditions, different types of lubricating oils (different compositions, different commercial makes…)

can exhibit similar responses relating the concentration of an element and the intensity of its emission. This is actually a question of the matrix effect. The ideal case is that a general calibration curve can be established for different oils provided that all the other experimental conditions are kept as identical as possible. Other important features for an advanced quantitative analytical technique correspond to the accuracy and the precision of the measurements, as well as the repeatability of the lasts for different operators and at different times. This paper therefore reports on the analysis of typical metallic elements, such as Fe, Cr and Ni, in virgin and used lubricating oils, in order to address the above raised critical points for an analytical technique.

2. Experimental

2.1. Sample preparation and collection

As shown in Table 1, 15 oils of different kinds were analyzed in this work. Among them, there were 10 virgin oils and 5 used lubricating oils. The 10 virgin oils consisted of a certified 75cSt blank oil (O1 in Table 1, from Techlab), 8 new lubricating oils (O2 to O9) of different types produced by 2 different lubricant manufacturers, and a cooking oil (O10). A multi-element metallo-organic standard containing 12 metallic elements (Fe, Cr, Ni, and Ag, Al, Cu, Mg, Na, Pb, Si, Sn, Ti) at a concentration of 550 μg/g (S1, from Techlab) and 3 single-element metallo-organic standards containing Fe, Cr and Ni respectively at 5000 μg/g (S2, from Conostan) were used to spike the virgin oils. Two sets of spiked virgin oils were prepared by weighing and mixing. The first set included the virgin oils, O1, O2, O3, O4 and O5. Among them O1 was spiked with S1 and the rest with S2 in order to get 5 series of laboratory-prepared reference samples containing 3 elements of interest Fe, Cr and Ni at 10 concentrations ranging from 20 μg/g to 550 μg/g. The second set of virgin oils labeled O6, O7, O8, O9 and O10, were spiked with S2 at 3 concentrations of Fe, Cr and Ni. These 3 concentrations were chosen as small, intermediary and high values and comprised between 20 μg/g and 300 μg/g, within the range of the calibration concentrations.

Five used lubricating oils were collected from a car service station. They were used oils of the 5 virgin oils mentioned above (O5 to O9). In order to keep the correspondence between the virgin and the used oils, we use in Table 1 the same number for a same kind of oil. The used one is then distinguished by adding the letter U (as used) to the name of the corresponding virgin oil. In Table 1, we provide as well the technical information, the specifications and the manufacturers of

Table 1
Substrate, standards and oil samples used or analyzed in this work with their characteristics and related useful information.

Type of sample	Name in this paper	Technical name	Specification	Provider	Contained elements[a]
Substrate	Target	Certified reference material	High purity aluminum block	TECHLAB	Al 99.99%, Cu 0.005%, Si 0.002%, Fe 0.001%
Standard	S1	Metallo-organic standard	12 elements in 75cSt base oil	TECHLAB	Fe, Cr, Ni, and Ag, Al, Cu, Mg, Na, Pb, Si, Sn, Ti at 550 μg/g
	S2		Single element, Fe, Cr or Ni	CONOSTAN	Fe, Cr, Ni at 5000 μg/g
Virgin lubricating oil	O1	75cSt base oil	75cSt blank mineral oil	TECHLAB	No Fe, Cr, Ni
	O2	Activa 5W40	Synthetic oil	Total	Mg, Si, Ca, Ti, Cu, Zn No Fe, Cr, Ni
	O3	Activa 10W40	Semi-synthetic oil		
	O4	Activa 15W40	Mineral oil		
	O5	Euro First C2 5W30	Synthetic oil	HAFA	Mg, Si, Ca, Ti, Cu, Zn No Fe, Cr, Ni
	O6	Euro First C1 5W30	Synthetic oil		
	O7	ECOTOURISME 10W40	Semi-synthetic oil		
	O8	Euro First C4 5W30	Synthetic oil		Fe, Mg, Si, Ca, Ti, Cu, Zn No Cr, Ni
	O9	Euro MAX 5W40	Synthetic oil		
Used lubricating oil	UO5	Euro First C2 5W30	IVECO 2.3 L Diesel, 68,000 km, 2008	Collected from garage	Fe, Cr, Mg, Si, Ca, Ti, Cu, Zn No Ni
	UO6	Euro First C15W30	FORD FOCUS 1.6 L Diesel, 96,000 km, 2008		
	UO7	ECOTOURISME 10W40	OPEL ASTRA Essence, 210,000 km, 1997		
	UO8	Euro First C4 5W30	RENAULT ESPACE 2 L DCI, 70,000 km, 2010		
	UO9	Euro MAX 5W40	RENAULT MEGANE 1.5 DCI, 80,000 km, 2004		
Cooking oil	O10	Cooking oil	Mixed vegetable oil (rapeseed, sunflower, grape seed)	Supermarket	Mg, Si, Ca, Ti, Cu No Fe, Cr, Ni

[a] Specified by the provider or detected in our laboratory within the limit of detection of the used setup. Note that the detected Cu and Si can also be contributed by the target.