Т. 86, № 1 **ЖУРНАЛ ПРИКЛАДНОЙ СПЕКТРОСКОПИИ** ЯНВАРЬ — ФЕВРАЛЬ 2019
V. 86, N 1 **JOURNAL OF APPLIED SPECTROSCOPY** JANUARY — FEBRUARY 2019

QUANTITATIVE ANALYSIS OF TRACE METALS IN ENGINE OIL USING INDIRECT ABLATION-LASER INDUCED BREAKDOWN SPECTROSCOPY

Junshan Xiu [1]*, Lili Dong [2], Yunyan Liu [1], Jiyuan Li [1]

[1] *School of Physics and Optoelectronic Engineering, Shandong University of Technology,*
Zibo, 255049, China; e-mail: xiujunshan@126.com
[2] *School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo, 255049, China*

In engine oil, the element composition and concentration changes as the engine operates. A rapid and effective detection of these changes, therefore, is needed to prevent accidents. Indirect ablation laser-induced breakdown spectroscopy (IA-LIBS) is a new technology introduced specially for oil samples. In this paper, 5 different oils are used for the analysis. The matrix effect on the calibration curves of analytical elements (Cu, Ti, Fe, and Ni) in these oils is investigated. The results show that the matrix effect is reasonably negligible under the conditions of our experiment. A generalized calibration curve can be established for analytical metals in different types of oils. We use the generalized calibration curves established to determine the concentrations of Cu, Ti, Fe, and Ni in mixed oils. The IA-LIBS results show that good agreement is obtained between the measured and known values.

Keywords: *indirect ablation LIBS, metals in engine oils, matrix effect, calibration curves.*

КОЛИЧЕСТВЕННЫЙ АНАЛИЗ СЛЕДОВ МЕТАЛЛОВ В МАШИННОМ МАСЛЕ С ИСПОЛЬЗОВАНИЕМ СПЕКТРОСКОПИИ ЛАЗЕРНО-ИНДУЦИРОВАННОЙ ПЛАЗМЫ

J. Xiu [1]*, L. Dong [2], Y. Liu [1], J. Li [1]

УДК 533.9;543.42

[1] *Школа физики и оптоэлектронной техники, Шаньдунский технологический университет,*
Цзыбо, 255049, Китай; e-mail: xiujunshan@126.com
[2] *Школа химии и химической инженерии, Технологический университет Шаньдун,*
Цзыбо, 255049, Китай

(Поступила 23 мая 2017)

Исследовано влияние матрицы на калибровочные кривые аналитических элементов Cu, Ti, Fe и Ni в пяти различных маслах. Показано, что это влияние пренебрежимо мало. Поэтому для металлов в различных типах масел может быть получена обобщенная калибровочная кривая. Представлены такие обобщенные калибровочные кривые для определения концентраций Cu, Ti, Fe и Ni. Результаты спектроскопии лазерно-индуцированной плазмы показывают хорошее соответствие между измеренными и известными концентрациями металлов в образцах.

Ключевые слова: *спектроскопия лазерно-индуцированной плазмы, металлы в моторных маслах, влияние матрицы, калибровочные кривые.*

Introduction. Quantitative analysis of traces of metals in viscous liquids has a number of applications, for example, in detecting heavy metal pollution due to petroleum spills [1, 2], monitoring lubricating oil in engines [3], or screening cooking oils for the presence of hogwash oils [4]. Such metals as Fe, Cu, Ni, Ti, Cr, and Al can be added into engine oil by contamination or by wear in an engine during its operation. Therefore, the monitoring and determination of the metal content in engine oils is essential to identify the adverse consequences of contamination in engines and avoid losses [5]. However, the complexity of the matrix as well as high viscosity and high organic loads represent serious challenges for analytical chemistry to deal with engine oils.

In general, indirect analytical procedures involving elaborate sample preparation are regarded as established techniques for the determination of metals in liquids. The associated analytical techniques are atomic absorption spectrometry (AAS) [6, 7], inductively coupled plasma optical emission spectrometry (ICP-OES) [8], the spectrophotometric method [9], and mass spectrometry (ICP-MS) [10]. Good analytical performance can be obtained with a limit of detection (LOD) in the range from 10 to 100 ng/g (ppb in weight) for the dilution factor of the initial oil [11]. However, the above-mentioned indirect analytical methods exhibit disadvantages not only because of the highly complex and expensive equipment but also because of the required expertise and the time-consuming preparation of the sample. This increases the cost of the analysis and prevents *in situ* or online monitoring and measurement. Therefore, direct determination of metals in liquids is required.

Laser-induced breakdown spectroscopy (LIBS), as a rapid, sensitive, and multi-element analysis method, has attracted more and more attention in recent decades [12, 13]. Moreover, LIBS has been applied successfully to detect metals in engine oils [12–17]. Due to the complex process of ablation for liquids, a lower detection sensitivity is produced in this case as compared with the solid sample [13, 18]. In our previous work, we introduced an indirect ablation LIBS method for which a thin film of oil was coated on the polished surface of a pure aluminum target. The laser pulse was focused slightly under the target surface. It transmitted through the transparent thin liquid layer and induced hot metallic plasma, which, in turn, ablated the thin oil film and excited the emissions of metals in the coating oil film [19]. Indirect ablation LIBS for the detection of metals in engine oils is investigated, and lower LODs, ranging from several ppm to several hundred ppb, level are demonstrated for various metals [20].

In this paper, we use indirect ablation LIBS for quantitative analysis of metals in engine oils. During the engine operation, the composition of the engine oil changes. This results in the changing matrix of the engine oil. Also, the matrix of oils in different engines, such as cars, ships, and aircraft, is different. The aim of this paper is to investigate the matrix impact on the results of measurements and to establish a generalized calibration curve for several metals in different oils. This paper represents the approach to the quantitative analysis of typical metallic elements, such as Cu, Ti, Fe, and Ni, in base oil and used engine oils.

Experimental. A standard LIBS setup is presented in Fig. 1. Its description can be found in [20]. Briefly, the fundamental output (1064 nm) of a Q-switched 10 Hz Nd:YAG laser is used for the ablation, the laser pulse energy being 90 mJ. The laser pulse is focused under the surface of the target with a shift of 1.5 mm by a lens of 50 mm focal length (L1). The target is mounted on motorized micrometric displacement stages with 3D displacement ability in order to provide a fresh oil layer for each laser pulse during the measurements. The distance between the focusing lens (L1) and the target surface is maintained constant during the measurement with a monitoring system consisting of a laser beam pointer and a monitoring CCD camera installed above the mirror M2. The small change of the height of the sample surface due to the presence of the oil layer on the target surface can be detected with the sample surface monitoring system. The thickness of the oil layers is estimated to be 15±5 μm. The plasma emission is collected by two lenses L2 and L3 with focal lengths 75 and 50 mm, respectively, and it is coupled into an optical fiber. The output of the fiber is connected with the entrance of a spectrometer, which is coupled with an intensified charge-coupled device camera (ICCD, iStar, Andor Technology). In our experiment, each spectrum is accumulated over 200 single laser shots realized in a matrix of 20×10 with the visible matrix of ablation craters (Fig. 1). The detection window is from 1.0 to 3.0 μs after the impact of the laser pulse on the target.

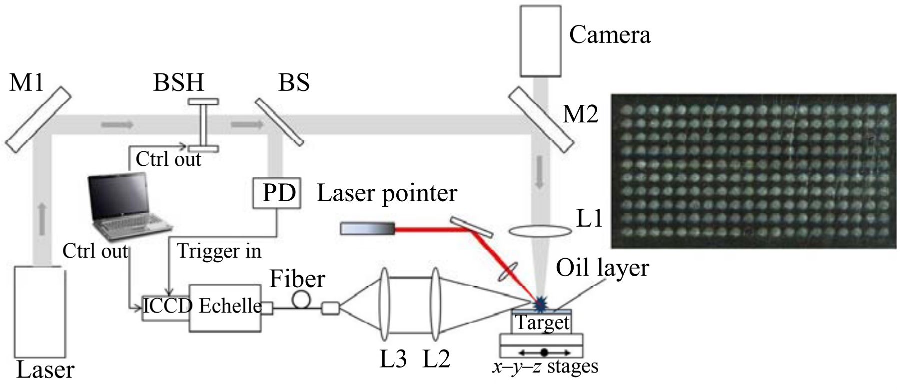

Fig. 1. Indirect ablation LIBS experimental set-up.

The two lubricating oils used in our work are collected from different ship engines, and the matrix compositions in them are different. We refer to the two oil samples as O1 and O2. Certified oil containing 12 metals (Ag, Al, Cr, Cu, Fe, Mg, Na, Ni, Pb, Si, Sn, and Ti) of 500 μg/g concentration in 75 cSt hydrocarbon base oil (Techlab, France) is used as the standard oil sample, named O3. Notice that we do not observe the spectral lines of Ag, Cr, Cu, Ni, Pb, Si, Sn, Fe, and Ti in both the O1 and O2 samples. In our work, we select Cu, Ti, Fe, and Ni as analytical elements. A set of reference samples is obtained by adding O3 into O1 and O2 with the metal concentration between 500 and 10 μg/g. The second set of oil samples labeled O4 and O5 is obtained by mixing O1 with O2 in varying proportions. For O4, the concentration ratio of O1 and O2 is 1:2. For O5, the ratio is 2:1. The matrix compositions in five oil samples are different. Two concentrations of Cu, Ti, Fe, and Ni are chosen as small and high values by adding O3 into O4 and O5 within the range of the calibration concentrations.

About 2 mL of the prepared sample is smeared with the help of a glass slide as uniformly as possible on the polished surface of a pure aluminum (Al 99.99%, Techlab, France) target to form a uniform thin layer. The thickness of the layer is 15±5 μm. The prepared sample is left for 3 min prior to the laser ablation for the oil layer to be stabilized on the target surface. After the analysis, the target surface can be cleaned and re-polished for use a new liquid sample. We can thus see that the entire sample preparation needs a very small quantity of liquid to be analyzed, a recyclable pure metallic substrate, the same basic laboratory tools, and less than 10 min of work. Such a procedure is very suitable for routine laboratory as well as field analysis.

Indirect ablation LIBS consists of an indirect breakdown of a thin layer of a viscous liquid on an aluminum target [19]. In this approach, the coating of the viscous liquid layer is prepared on the surface of the aluminum target. A laser pulse is focused slightly under the surface of the target, which induces hot aluminum plasma (Fig. 2a). The interaction between the aluminum plasma and the layer leads to an indirect breakdown of the layer (Fig. 2b). After the evolution of the plasma, one gets a mixture of the aluminum plasma and the layer plasma at a very high temperature for the sensitive detection of elements contained in the layer (Fig. 2c). The characteristics of indirect ablation plasma are described in detail in [19].

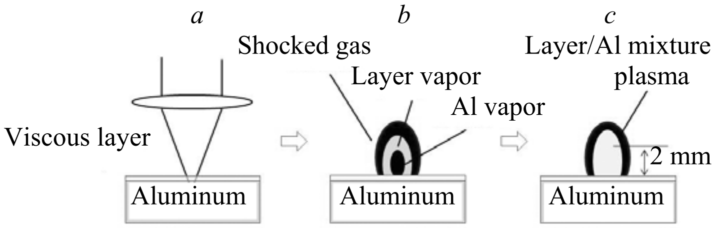

Fig. 2. The evolution of the plasma induced by indirect ablation LIBS.

TABLE 1. Limits of Detection of Metals in Engine Oils with This Approach and Other Approaches

Element	LOD (μg/g) Al substrate	LOD (μg/g) FP, single* [21]	LOD (μg/g) FP, double** [21]
Cu	2.87	4.00	1.00
Ag	1.50	2.00	1.00
Ti	3.20	5.00	2.00
Si	9.71	19.00	11.00
Cr	10.59	29.00	12.00
Ni	10.73	20.00	7.00
Fe	3.73	4.00	3.00
Mg	0.29		
Sn	11.59		

* Filter paper substrate with single pulse LIBS.

** Filter paper substrate with double pulse LIBS.

When the laser pulse is focused slightly under the target surface, it transmits through the transparent thin liquid layer and induces hot metallic plasma. The last one is confined by the liquid layer in its early stage of propagation. The interaction between the metallic vapor and the liquid layer leads to the vaporization and ionization of the layer. At a delay of about 1 μs after the laser pulse impact, plasma is observed with a mixture of species from the metallic target as well as the liquid layer. A temperature as high as 15000 K is observed for the mixture plasma. It allows a high excitation energy emission from the elements. The emission from the elements evaporating from the oil layer is maximal at a height of 2.0 mm with respect to the sample surface. This is why a fiber is put inside the plasma. Limits of detection from several ppm to hundreds ppb are demonstrated for various metals (Table 1 [21]).

Results and discussion. *Single calibration curves of metals in different oils.* Emission spectra are recorded for 3 sets of laboratory-prepared oil samples (O1, O2, and O3) with the setup and protocol described above. The representative lines for the quantitative analysis of the four elements are selected as Cu I 324.7 nm, Ti II 334.9 nm, Fe II 259.9 nm, and Ni I 352.45 nm, according to the criterion shown in [21]. The emission intensities of the 4 representative lines of the 4 elements are then extracted from the spectra by fitting the line profiles with a polynomial function. In order to average the shot-to-shot fluctuation of the laser energy, we use the C I 247.9 nm line as an internal reference to normalize the emission intensities of the analyzed elements. Such a choice is reasonable for an organic matrix, such as oil. The concentrations of Cu and Ti in the oils samples are selected in the lower level (<100 ppm) due to a higher detection sensitivity than the other two elements Fe and Ni. The obtained calibration curves are shown in Fig. 3. In this figure, the data points represent the mean values of the line intensities resulting from the 8 replicate measurements. The error bars represent the associated standard deviations (±σ).

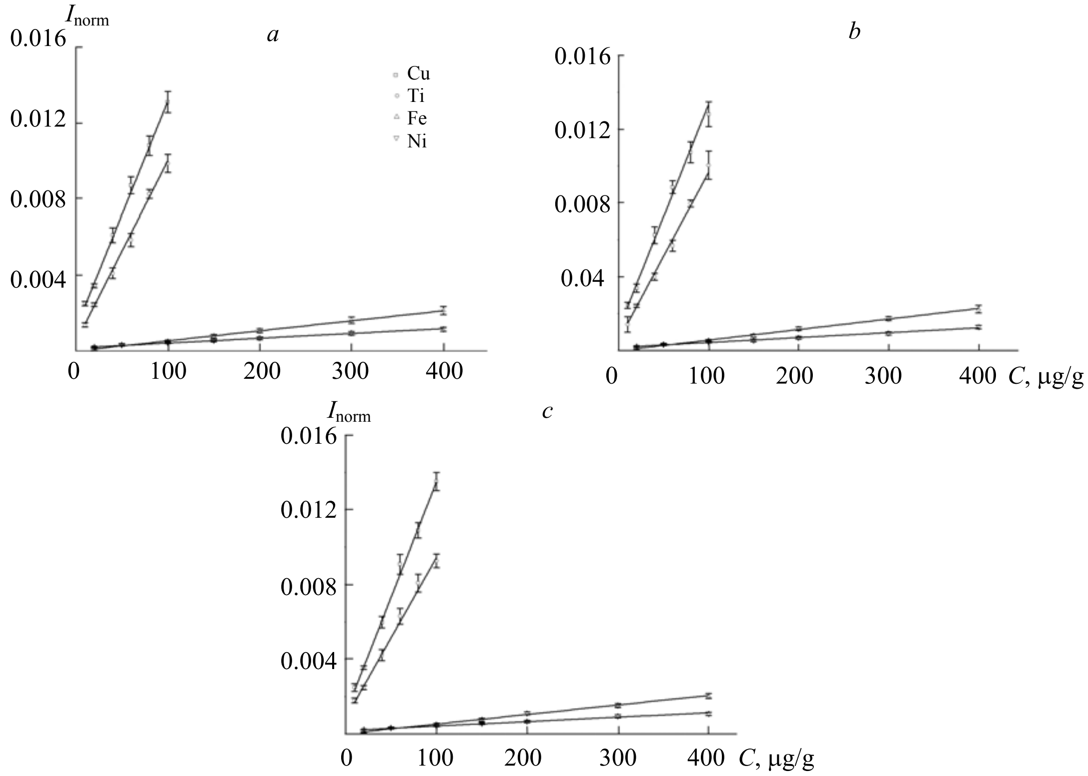

Fig. 3. Calibration curves of Cu, Ti, Fe, and Ni for the three oil samples O1 (a), O2 (b), and O3 (c).

The fitting parameters for the 4 elements (Cu, Ti, Fe, and Ni) detected in the 3 oil samples are provided in Table 2. From the data shown in Table 2, we can see that the calibration curves established for the 3 sets of oil samples present similar slopes for the 4 analyzed elements. This means that the matrix effect between the different oils is small and reasonably negligible under the conditions of our experiment. Such remarkable behavior is believed to be due to the fact that the characteristics of the plasma are mainly determined by the aluminum plasma directly induced by the laser pulse on the oil film coated on the target surface. Such performance demonstrates clearly the reliability and stability of the LIBS measurements with the developed experimental setup and protocol. We remark finally that the correlation of the experimental data with linear regressions is always very good and the linear fitting coefficients are all superior to 0.99. The similitude between the calibration curves established with the three oils samples suggests that a universal calibration curve can be built for each analyzed element. Such a calibration curve can take into account the matrix of an ensemble of different types of oil and be used for the element determination in these samples.

TABLE 2. Fitting Parameters Extracted with Linear Regression of The Individual Data Measured with the Three Oils for Cu, Ti, Fe, and Ni

Element	Parameter	Sample O1	Sample O2	Sample O3	Relative deviation, %
Cu	a	1.06×10^{-3}	1.19×10^{-3}	1.17×10^{-3}	6.98
	s	1.25×10^{-4}	1.19×10^{-4}	1.21×10^{-4}	2.30
	R^2	0.998	0.994	0.993	–
Ti	a	7.47×10^{-4}	4.82×10^{-4}	5.63×10^{-4}	28.5
	s	8.89×10^{-5}	9.52×10^{-5}	9.10×10^{-5}	1.65
	R^2	0.995	0.996	0.995	–
Fe	a	1.04×10^{-5}	7.01×10^{-6}	1.75×10^{-5}	46.0
	s	5.29×10^{-6}	5.71×10^{-6}	5.12×10^{-6}	5.65
	R^2	0.994	0.993	0.994	–
Ni	a	1.71×10^{-4}	1.73×10^{-4}	1.89×10^{-4}	5.55
	s	2.53×10^{-6}	2.64×10^{-6}	2.36×10^{-6}	5.62
	R^2	0.996	0.995	0.993	

Generalized calibration curves established for each element. In order to check how close are the calibration curves built with 3 sets of laboratory-prepared oils, we merge the ensemble of the line intensities measured for the 3 sets of oils in order to build generalized calibration curves for the 4 elements (Cu, Ti, Fe, and Ni). More precisely, in such a procedure, 4 calibration curves are plotted respectively for the 4 elements, as shown in Fig. 4. The fitting parameters extracted with linear regression of the data are provided in Table 3. We can see in Fig. 4 that the merged data show a high linear correlation. The linear fitting coefficients for the 4 elements are all larger than 0.99. This demonstrates the negligible matrix effect between the different oils, as we already mentioned above. The fitting parameters presented in Table 3 and Table 2 show little difference in the slopes between the calibration curves established with the merged data and each value of the slopes calculated from the individual oil data. The difference of the intercept is also much reduced, as compared with the case of the data for individual oils.

TABLE 3. Fitting Parameters Extracted with Linear Regression of the Merged Data Measured with Three Oils for Cu, Ti, Fe, and Ni

Parameter	Cu	Ti	Fe	Ni
a	1.19×10^{-3}	5.75×10^{-4}	7.00×10^{-6}	1.79×10^{-4}
s	1.23×10^{-4}	9.26×10^{-5}	5.37×10^{-6}	2.50×10^{-6}
R^2	0.994	0.996	0.991	0.993

Accuracy of the concentration determination in the prepared samples. We use the established generalized calibration curves to determine the concentrations of Cu, Ti, Fe, and Ni in mixed oils O4 and O5. The nominal concentrations used for the preparation of the samples are considered as the reference concentrations in our experiment to evaluate the accuracy and precision of the concentration determination using the setup and protocol described above. The obtained results are presented in Fig. 5. We can see in Fig. 5 that the concentrations for the oil samples are determined with the calibration curves established with the merged data of 2 sets of the laboratory reference samples (merged), as well as with the calibration curves established with the 75cSt base oil (base oil), for comparison. The determined concentrations together with their uncertainty (standard deviation) are represented in Fig. 5. Good agreement is obtained between the calculated from the generalized calibration curves and the reference values. It indicates that our method is suitable for quantitative analysis of trace metals elements in engine oils samples of different types. Also it is possible to extend the validity of the generalized calibration curves established with engine oils to other kinds of oils.

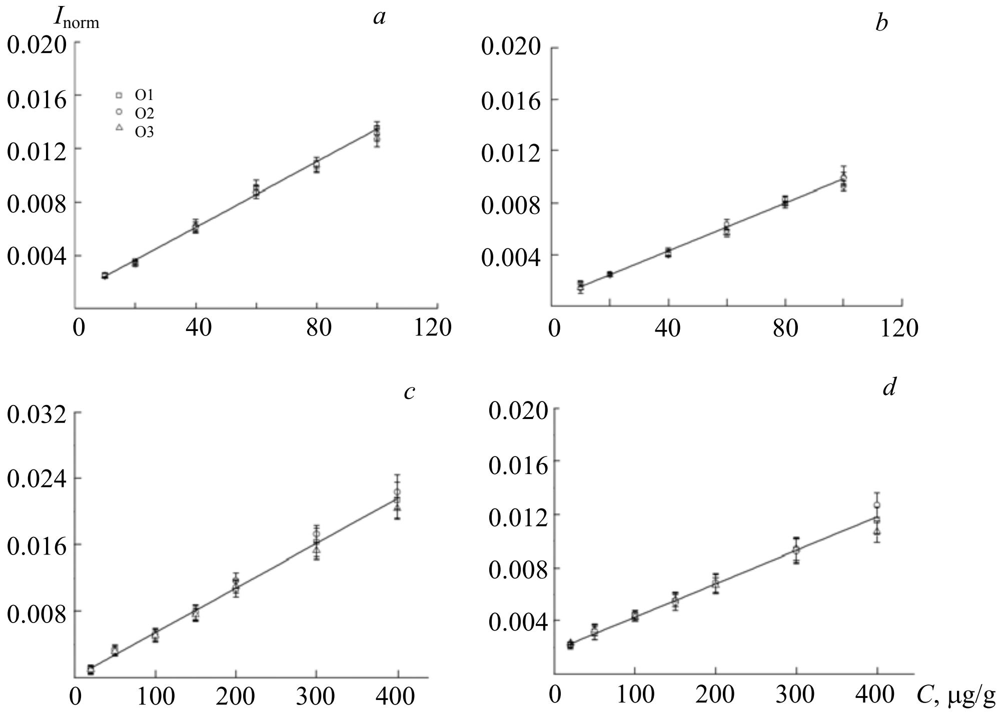

Fig. 4. Generalized calibration curves with the merged data obtained from three oils (O1, O2, and O3) for Cu (a), Ti (b), Fe (c), and Ni (d).

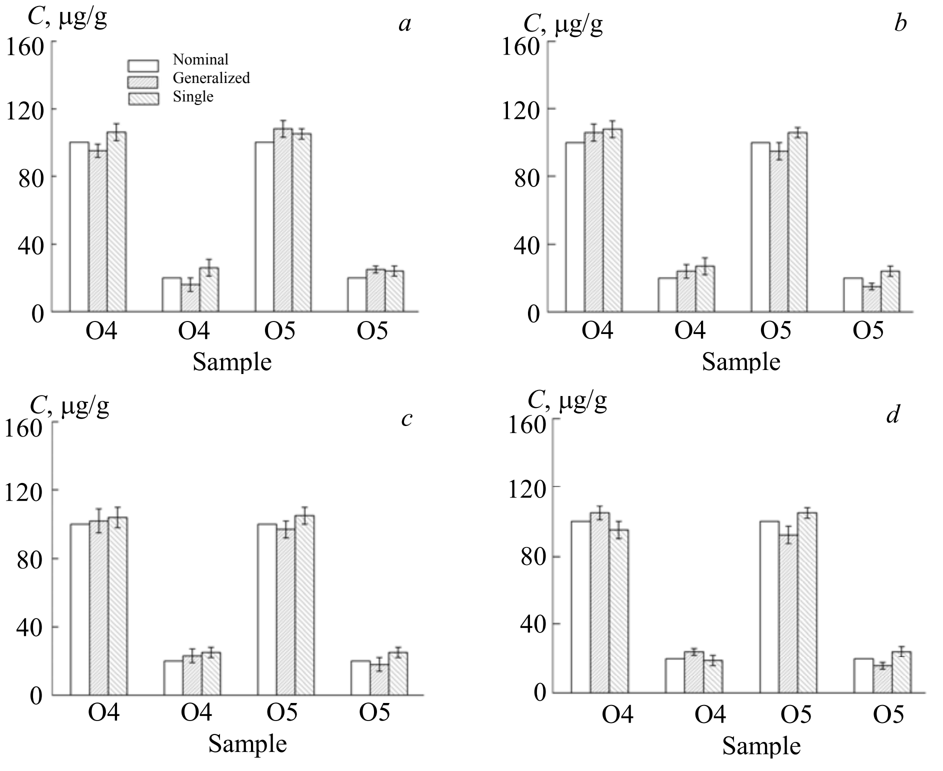

Fig. 5. Determination of the concentrations of Cu (a), Ti (b), Fe (c), and Ni (d) in oils O4 and O5 with the use of two sets of calibration curves. The first one is established with the merged data (generalized), and the second one is obtained with the data from the 75cSt oil (single). The nominal values of the concentrations (Nominal) are also presented as references.

Conclusion. A specific configuration of indirect ablation LIBS for trace metals in engine oils is herein investigated. The main objective of this work is to address the quantitative analysis of trace metals in different types of engine oils. Our results show that the calibration curves established with different types of oils exhibit a similar behavior. This means that the matrix effect between the different oils is quite small and reasonably negligible under the conditions of our experiment. Generalized calibration curves can be established for trace metals in different types of oils. We have evaluated the accuracy of our measurements, and good agreement has been obtained between the calculated from the generalized calibration curves and the reference values. For indirect ablation LIBS, the oils are smeared as uniformly as possible on the polished surface of a pure metallic substrate to form a uniform thin layer. We believe that such a negligible matrix effect observed in our experiment is due to the fact that the properties of the plasma are mainly determined by the metallic plasma directly induced by the plasma pulse. This indicates that our method is suitable for quantitative analysis of trace metals elements in oils samples of different types with accurate results. Indirect ablation LIBS provides a feasible and sensitive method for rapid detection of trace metals in viscous liquids.

Acknowledgment. Financial support from the National Natural Science Foundation of China (Grant No. 11704228) and the Shandong Provincial Natural Science Foundation (ZR2016AQ22) is highly acknowledged. The authors thank the French Centre National de Recherche Scientifique and the National Natural Science Foundation of China for their support to the international collaboration and exchange program.

REFERENCES

1. M. A. Gondal, T. Hussain, Z. H. Yamani, M. A. Baig, *Talanta*, **69**, No. 5, 1072–1078 (2006).
2. J. O. Nriagu, J. M. Pacyna, *Nature*, **333**, No. 6169, 134–139 (1998).
3. R. Q. Aucélio, R. M. de Souza, R. C. de Campos, N. Miekeley, C. L. P. da Silveira, *Spectrochim. Acta B*, **62**, No. 9, 952–961 (2007).
4. Y. H. Wei, J. Y. Zhang, T. C. Dai, T. H. Tu, L. G. Luo, *Food Sci.*, **32**, No. 12, 213–215 (2011).
5. K. J. Eisentraut, R. W. Newman, C. S. Saba, R. E. Kauffman, W. E. Rhine, *Anal. Chem.*, **56**, No. 9, 1086A–1091A (1984).
6. B. F. Reis, M. Knochen, G. Pignalosa, N. Cabrera, J. Giglio, *Talanta*, **64**, No. 5, 1220–1225 (2004).
7. A. V. Zmozinski, A. de Jesus, M. G. R. Vale, M. M. Silva, *Talanta*, **83**, No. 2, 637–643 (2010).
8. R. M. Souza, C. L. P. da Silveira, R. Q. Aucélio, *Anal. Sci.*, **20**, No. 2, 351–355 (2004).
9. G. M. Mastoi, M. Y. Khuhawar, R. B. Bozdar, *J. Quant. Spectrosc. Radiat. Transfer*, **102**, No. 2, 236–240 (2006).
10. M. P. Escobar, B. W. Smith, J. D. Winefordner, *Anal. Chim. Acta*, **320**, No. 1, 11–17 (1996).
11. I. M. Goncalves, M. Murillo, A. M. Gonzalez, *Talanta*, **47**, No. 4, 1033–1042 (1998).
12. P. Celio, C. Juliana, M. C. S. Lucas, B. G. Fabinao, *J. Braz. Chem. Soc.*, **18**, No. 3, 463–512 (2007).
13. A. De Giacomo, M. Dell'Aglio, O. De Pascale, M. Capitelli, *Spectrochim. Acta B*, **62**, No. 8, 721–738 (2007).
14. P. Fichet, P. Mauchien, J. F. Wagner, C. Moulin, *Anal. Chim. Acta*, **429**, No. 2, 269–278 (2001).
15. C. A. D'Angelo, M. Garcimuño, D. M. D. Pace, G. Bertuccellil, *J. Quant. Spectrosc. Radiat. Transfer*, **164**, 89–96 (2015).
16. F. Boué-Bigne, *Spectrochim. Acta B*, **63**, No. 10, 1122–1129 (2008).
17. J. Kaiser, M. Galiová, K. Novotný, R. Červenk, L. Reale, J. Novotný, M. Liška, O. Samek, V. Kanický, A. Hrdličk, K. Stejskal, V. Adam, R. Kizek, *Spectrochim. Acta B*, **64**, No. 1, 67–73 (2009).
18. F. Y. Yueh, R. C. Sharma, J. P. Singh, H. S. Zhang, W. A. Spencer, *Air Waste Manage.*, **52**, No. 11, 1307–1315 (2002).
19. J. S. Xiu, X. S. Bai, E. Negre, V. Motto-Ros, J. Yu, *Appl. Phys. Lett.*, **102**, No. 102, 2441011–2441015 (2013).
20. J. S. Xiu, V. Motto-Ros, G. Panczer, R. E. Zheng, J. Yu, *Spectrochim. Acta B*, **91**, 24–30 (2014).
21. P. Yaroshchyk, R. J. S. Morrison, D. Body, B. L. Chadwick, *Spectrochim. Acta B*, **60**, No. 11, 1482–1485 (2005).