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ANALYSIS OF NONMETALLIC CONSTITUENTS OF LUBRICATING OIL USING INDIRECT ABLATION LASER INDUCED BREAKDOWN SPECTROSCOPY[**]

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Indirect ablation laser induced breakdown spectroscopy (IA-LIBS) was applied to the analysis of the nonmetallic constituents of engine oil and considered as a feasible technique for the evaluation of the consumption and/or combustion of engine oil during routine engine operation. The evolution of CN emission and C_2 emission was investigated for different driving time intervals of the motor. The exponentially decaying curve showed that the intensity of CN emission and C_2 emission decayed at different driving time intervals. The evolution of total CN emission and C_2 emission was analyzed, and the ratio of CN to C_2 was calculated, which might be taken as an indicator to evaluate the performance of the used engine oils and/or to diagnose the conditions of the motor engine. Thus, it is shown that IA-LIBS is a potential method for analyzing the metallic and nonmetallic constituents of engine oil.

Keywords: *indirect ablation laser induced breakdown spectroscopy, engine oil, emission line.*

АНАЛИЗ НЕМЕТАЛЛИЧЕСКИХ СОСТАВЛЯЮЩИХ СМАЗОЧНОГО МАСЛА С ПОМОЩЬЮ ЛАЗЕРНО-ИСКРОВОЙ СПЕКТРОСКОПИИ С КОСВЕННОЙ АБЛЯЦИЕЙ

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Для анализа неметаллических составляющих моторного масла применена лазерная спектроскопия с косвенным абляционным воздействием (IA-LIBS), которая рассматривается в качестве возможного метода оценки потребления и/или сгорания моторного масла во время работы двигателя. Исследована эволюция излучения CN и C_2 при разном времени работы двигателя. Кривая экспоненциального затухания показывает, что интенсивность излучения CN и C_2 уменьшается в разные интервалы времени вождения. Проанализирована эволюция общего выброса CN и C_2. Рассчитано отношение объемов выбросов CN к C_2, которое можно использовать в качестве показателя для оценки эффективности применения моторных масел и/или для диагностики состояния двигателя. Показано, что IA-LIBS – потенциальный метод анализа металлических и неметаллических компонентов моторного масла.

Ключевые слова: *спектроскопия лазерного пробоя, моторное масло, линия испускания.*

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Introduction. Lubricating oil plays an important role in the normal operation of the motor. It is composed of hydrocarbons and nitrile compounds containing one or more cyano groups (-C=N). During engine operation, wear is unavoidable because it has both physical (friction between metallic parts causing high temperature and pressure) and chemical (corrosion) reasons. Chemical wear may produce not only metallic particles but also soluble metallo-organic species, whereas physical wear is generated by metallic particles of varying sizes (up to a few micrometers) [1, 2].

Some metallic elements need to be added to virgin lubricating oil to improve its capacity and achieve antioxidative, anticorrosive, dispersing, antiwear, or other properties. Such compounds involve a large number of elements, such as Mg, Si, Ca, Zn, and Ba [3]. However, the used engine oil may contain gasoline, additives (detergents, dispersants, oxidation inhibitors, rust inhibitors, and viscosity improvers), nitrogen and sulfur compounds, and a broad range of aromatic and aliphatic hydrocarbons with chain lengths ranging from C 15 to C 50, in addition to metals [4]. The used engine oil undergoes heating, friction, oxidation, and combustion when the motor is operating, which may generate higher percentages of polycyclic aromatic hydrocarbons (PAHs) and additives [5, 6]. For example, hydrocarbon molecules will react to incorporate oxygen atoms into their structure over time. This reaction produces acids, sludge, and varnish that foul or damage metallic parts. The compositions of engine oil are always changing with the engine operating, which can affect the performance of engine oil. Therefore, monitoring and determining the composition and concentration of elements in lubricating oils, which may come from either metallo-organic compounds or nonmetallic constituents, would provide an efficient way to alert and diagnose any defective functioning in oil-lubricated engines, and, if possible, before failures occur [7].

However, the complexity of the matrix, high viscosity, and high organic loads bring serious challenges in using analytical chemistry to deal with engine oils. In general, indirect analysis procedures involving an elaborated sample preparation are considered as established techniques for the determination of elements in liquids. The common associated analytical techniques are atomic absorption spectrometry (AAS) [8, 9], inductively coupled plasma optical emission spectrometry (ICP-OES) [10], the spectrophotometric method [11], or mass spectrometry (ICP-MS) [12]. However, the above established indirect analytical methods exhibit disadvantages not only in the highly complex and expensive equipment, but also in the required expertise and long time for reliable sample preparation. They increase the cost of the analysis and prevent in situ or online monitoring and measurement. Therefore, direct determination of elements in oils is required to satisfy the need for fast analysis.

Laser induced breakdown spectroscopy (LIBS) technology, as a rapid, online, sensitive and multi-element analysis method, has gotten more and more attention in recent decades [13, 14]. Moreover, LIBS has been applied successfully to the detection of metals in engine oils [13–19] and the analysis of nonmetallic constituents in crude [20] or engine oil [4]. In our previous work, we introduced an indirect ablation LIBS (IA-LIBS) configuration where 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 and transmitted through the transparent thin liquid layer, which induced a dense and hot metallic plasma. Then the hot metallic plasma ablated the thin oil film and excited the emissions of metals in the coating oil film [21]. The quantitative analysis of trace metal elements in engine oils was achieved by IA-LIBS [22, 23]. The matrix effect in different oils was also studied [23, 24], and the lower LODs ranging from several ppm to hundreds of ppb were demonstrated for various metals [22].

In this paper, an extensive investigation of indirect ablation LIBS for the analysis of nonmetallic constituents in engine oils was conducted. Used engine oil samples collected from the same motor with different driving time intervals were detected by IA-LIBS. The evolution of cyanide (CN) emission and carbon molecular (C_2) emission from used engine oil samples was explored. Our aim was to evaluate the performance of used engine oils and/or to diagnose the conditions of the motor engine based on the evolution of cyanide (CN) emission and carbon molecular (C_2) emission in used engine oils.

Experiment. *Experimental setup.* A standard LIBS setup was used in this experiment (Fig. 1). Its detailed description can be found elsewhere [21, 25]. Briefly, the fundamental output (1064 nm) of a *Q*-switched Nd:YAG laser operating at 5 Hz was used for ablation with a laser pulse energy of 90 mJ delivered to the sample. The laser pulse was focused slightly on the sample surface by a lens of 50 mm focal length (L1). The lens-to-sample distance was monitored to be constant for the translation of the target, where a system combining a laser pointer in oblique incidence on the target surface and a monitoring camera was used. A pair of tubes was placed above the target to bring a stream of argon gas with a fixed flow of 8 L/min, which ensured the plasma to expand into a pure argon ambient at a 1 atm pressure (not shown in Fig. 1).

The plasma emission was collected by a combination of two lenses L2 and L3 with a focal length of 100 mm and 50 mm, respectively, and it was coupled to an optical fiber. The output of the fiber was connected to the entrance of a spectrometer (Andor, Mechelle 5000), which was in turn coupled to an intensified charge-coupled device camera (ICCD, iStar, Andor Technology). The detection system offered a spectral range 220–850 nm with a resolution of $\lambda/\Delta\lambda = 5000$. Each spectrum was recorded by the accumulation of over 200 single-shot ablations at 200 different craters. A photodiode was used to detect the part of the laser pulse that provided the trigger signal for the ICCD camera. The detection window was set from 1.0 to 3.0 μs after the impact of the laser pulse on the target. The experimental condition, including the laser parameters and detection parameters such as the detection gate and the gain applied to the ICCD, were kept similar for all the samples.

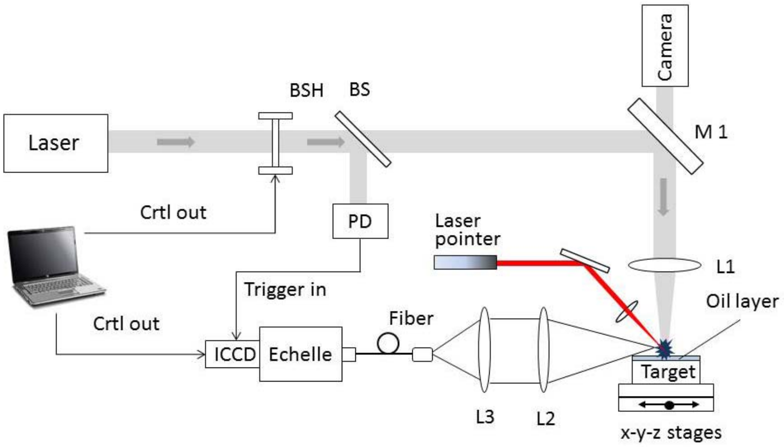

Fig. 1. Schematic diagram of the LIBS experimental setup.

Sampling. In our experiment, one virgin lubricating oil sample (pure synthetic engine oil) and seven used lubricating oil samples were obtained from an authorized car service station. Used lubricating oil samples were collected from the same car which had been steered in different time intervals. We remark that one usually changes lubricating oil after 5000 km of mileage or six months of driving time. However, car driving mileage is usually less than 5000 km, whereas the driving time is more than six months. In order to determine the performance of engine oil in different driving time intervals, the seven used engine oil samples were collected when the same car's driving time was zero, three, six, seven, eight, nine, ten, and twelve months, respectively. About 10 ml of each oil sample was collected in a dark glass bottle.

About 2 ml of the prepared sample was smeared with the help of a glass slide as uniformly as possible on the polished surface of a pure aluminum (Al 99.99%) target to form a uniform thin layer. The prepared film was left for 10 min to get a more uniform and stable distribution of the oil on the target surface before laser ablation. The thickness of the oil layer was estimated to be 15 ± 5 μm as reported in our previous works [21–24]. The detailed sampling procedure can be found elsewhere [22, 23].

Results and discussion. *IA-LIBS raw spectroscopy and representative lines.* In order to obtain high analysis performance, the selection of a sensitive and suitable spectral line for each emission to be detected is very important. In this work, the echelle spectrometer was used to record the emission spectrum from the virgin lubricating oil sample over a wide spectral range 220–850 nm. Figure 2 shows the IA-LIBS spectra of the virgin lubricating oil sample for nonmetallic constituents with different spectral emission regions including the CN molecular band, the C_2 molecular band, and the N atomic emission. In Fig. 2, two CN molecular band emissions can be observed near 388 and 421 nm, three C_2 molecular band emissions can be observed near 473, 516, and 563 nm, and three nitrogen atomic emissions could be observed at 742.36, 744.23, and 746.83 nm. The selected lines were relatively intense for the corresponding element under the given conditions of ablation and detection. They were chosen to be as free as possible from any interference from other spectral features. Another important criterion is that the line should not be affected by self-absorption. In this work, according to the criteria above, the strongest spectral lines of each emission in each spectral region were selected. The CN lines were selected finally as 388.31 and 421.58 nm, C_2 lines were selected as 473.67, 516.48, and 563.47 nm, and the N atomic line was selected as 746.83 nm.

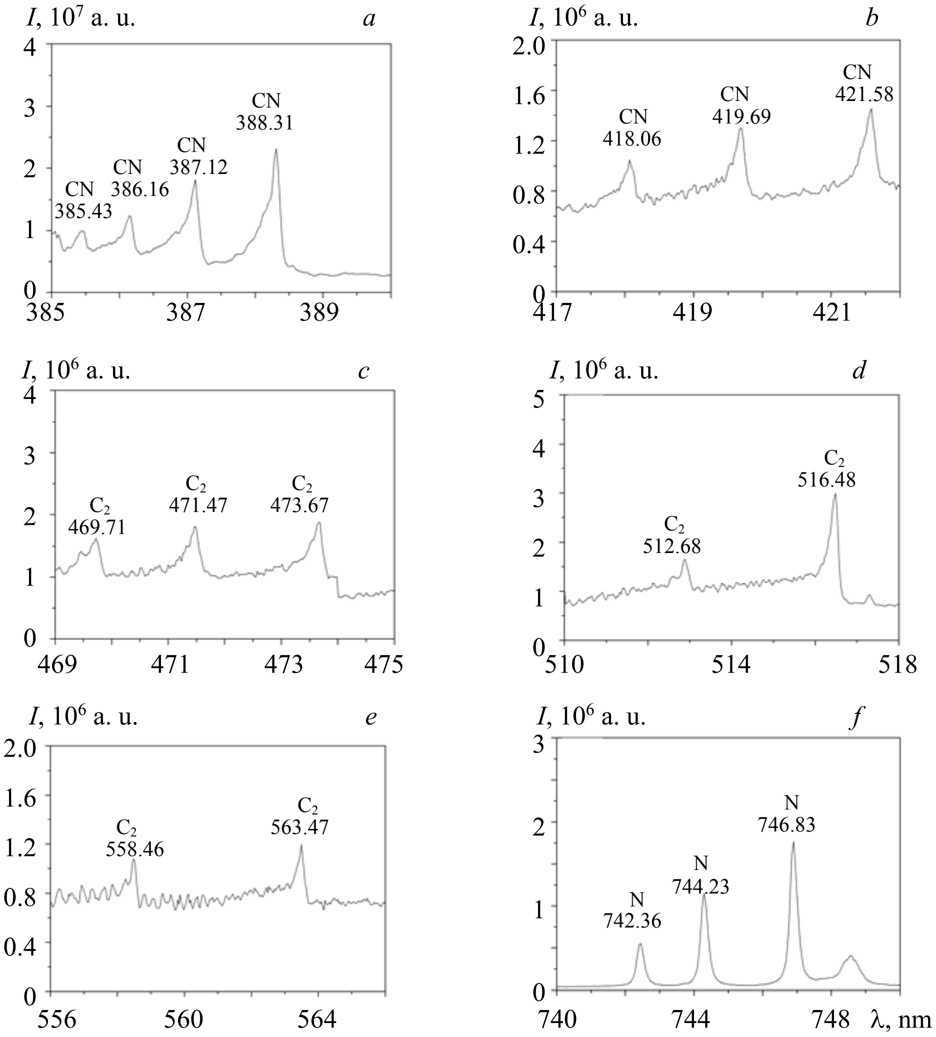

Fig. 2. IA-LIBS spectra of the virgin lubricating oil sample for nonmetallic constituents with different spectral emission regions including that of the CN molecular band (a, b); the C_2 molecular band (c, d, e), and the N atomic emission (f).

In order to average the shot-to-shot fluctuation of the laser energy and avoid any unwanted experimental fluctuation, we used the C I 247.86 nm line as an internal reference to normalize the emission intensity of each analyte. The C I 247.86 nm line as an internal reference was available to IA-LIBS for different types of oils [22–24]. In our work, all emission intensities were normalized against the intensity of the C I 247.86 nm spectral line.

Emission evolution of nonmetallic constituents in used lubricating oils. The composition of engine oils including trace metallic elements and nonmetallic constituents is always changing during the normal operation of the engine. Nonmetallic constituents such as hydrocarbons and cyano groups are subject to chemical deterioration under normal operating conditions of the engine. However, a wide variety of byproducts such as ketones, esters, aldehydes, carbonates, and carboxylic acids might be produced during the degradation and combustion process of engine oil. The exact distribution and composition of these byproducts are complex, and they contributed effectively to the depletion of basic lubricating properties of the oil [26]. In order to determine the performance of engine oil under normal operation of the engine at an early stage, eight engine oil samples were detected from the same engine with different driving time intervals of zero, three, six, seven, eight, nine, ten, and twelve months. Figures 3 and 4 show the lines representing the evolution of CN and C_2 emissions (not N element emission) in engine oil samples at different driving time intervals. We remarked that the emission intensity evolution of the N element was not fitted to certain function, and it may change irregularly due to complicated chemical decomposition in engine oil during the normal operation of the engine. As shown in the figures, the spectral intensity was normalized with the reference line intensity of the C I 247.86 nm. The error bars represent the associated standard deviations of the experimental data. The curves of the experimental points in Figs. 3 and 4 can be fitted to a nonlinear function:

$$y = y_0 + Ae^{Bx}, \quad (1)$$

where x represents the driving time intervals, and y is the relative intensity of the emission line. The nonlinear parameters of the fitting curves are provided in Table 1.

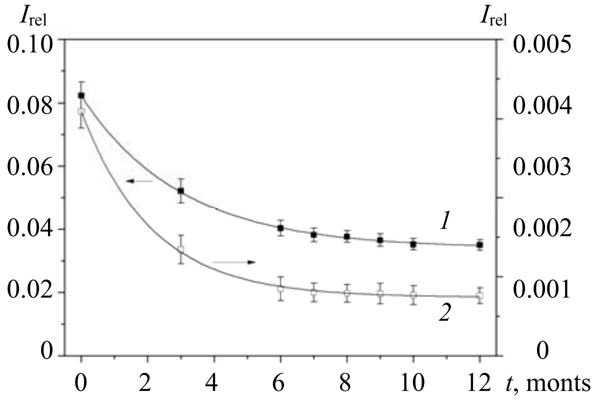

Fig. 3. The evolution of the normalized intensities for CN emission at representative lines of 388.31 (1) and 421.58 nm (2) under different driving time intervals.

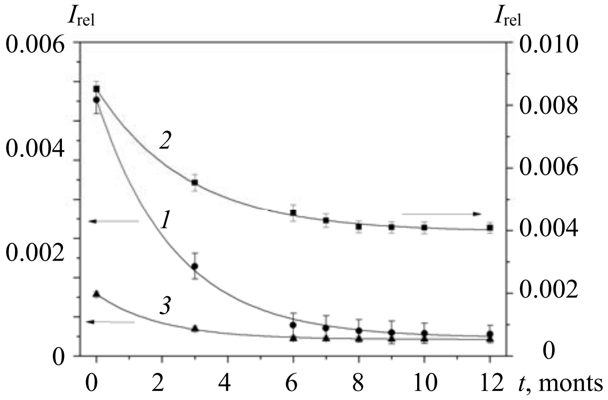

Fig. 4. The evolution of the normalized intensities for C_2 emission at representative lines of 473.67 (1), 516.48 (2), and 563.47 nm (3) under different driving time intervals.

TABLE 1. Fitting Parameters of the Experimental Data Corresponding to the Fitting Curves

Emission lines, nm	y_0	A	B	R^2
CN 388.31	0.3391	0.4836	–0.3329	0.998
CN 421.58	0.0074	0.0236	–0.4726	0.998
C_2 473.67	0.0396	0.0455	–0.3597	0.997
C_2 516.48	0.0305	0.0305	–0.4228	0.997
C_2 563.47	0.0052	0.0145	–0.4991	0.998

Note. The parameters are defined according to Eq. (1).

In Fig. 3, we can see that the intensity of the CN emission decayed at different driving time intervals following the exponentially decaying curve equation shown above. The fitting coefficients are all superior to 0.99, as listed in Table 1. It indicated that the chemical bonds of the hydrocarbons and cyanide groups in engine oil were dissociated under friction and high temperature during the normal operation of the engine. A similar evolution of the C_2 emission can be observed in Fig. 4, showing that molecular carbon was dissociated because of heating, contamination, and oxidation of engine oil under engine operation.

The evaluation of lubricating oil performance. As shown in Figs. 3 and 4, the CN and C_2 emissions of the representative spectral lines display a similar evolution behavior. We plotted the evolution of the normalized intensities of all CN and C_2 emissions in the spectral emission of oil samples at different driving time intervals, as shown in Fig. 5. The fitting parameters of the curves are listed in Table 2. As shown in Fig. 5, the number of CN and C_2 molecules decayed gradually after certain driving time intervals. When the driving time interval was three months, the number of CN and C_2 molecules decayed to 39.3 and 41.2%, respectively, of the largest value from the virgin oil at month zero. When the time interval was six months, the decay was about 50%, and it was variable more or less when the driving time intervals were more than six months. This shows that the chemical bonds of the hydrocarbons and cyanide groups in engine oils decreased sharply when the driving time intervals were before six months (half a year), and decreased less with the increasing time intervals. The obtained results indicated that during normal degradation or consumption of engine oil (oxidization, heating, chemical breakdown, and contamination), the performance of the engine oils was degraded and deteriorated as the driving time intervals increased.

TABLE 2. Fitting Parameters of the Experimental Data Corresponding to the Fitting Curves Shown in Figs. 5 and 6

Emissions	y_0	A	B	R^2
CN	0.7749	1.3034	–0.3533	0.995
C_2	0.0843	0.1615	–0.3610	0.995
CN/C_2	9.3358	–0.8931	–0.1286	0.985

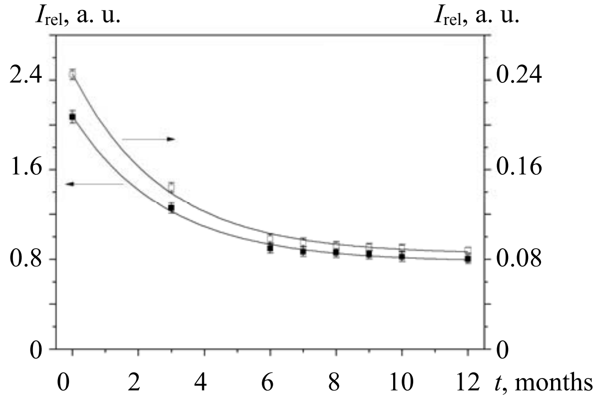

Fig. 5. The evolution of the normalized intensities of all CN (■) and C_2 (□) emissions of oils samples at different driving time intervals.

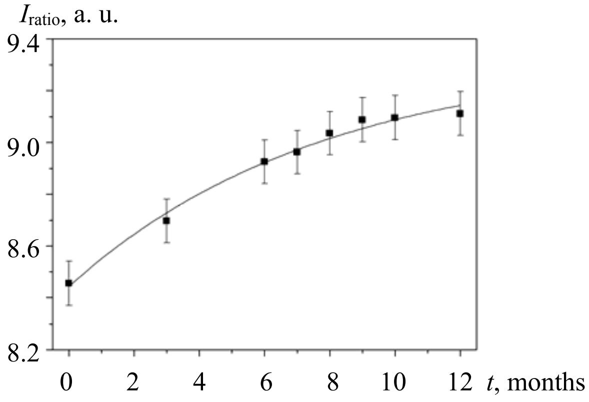

Fig. 6. The trends of the intensity ratio of CN and C_2 emissions at different driving time intervals.

The results above showed that both CN and C_2 emissions decayed gradually after certain driving time intervals during engine operation, with obvious differences in the rationed intensities. CN molecules in nitrile compounds displayed high dissociation sensitivity under extreme conditions during the degradation and combustion process of engine oil, and C_2 molecules mainly from the aromatic were dissociated because of heating and oxidation of lubricating oil during engine operation [4, 20]. The heating, oxidation, and aging of oil could cause a different distribution in the content of aliphatic and aromatic hydrocarbon, as well as the changes in the organic fraction (CN and C_2) [20]. The changing process of the oil statues could be explained by the variations of the ratio of CN/C_2 [20]. In this work, we calculated the ratio of total CN emissions to C_2 emissions in order to offer additional information on the engine oil performance of the used engine oils. Figure 6 shows the trends of the intensity ratio of CN emission to C_2 emission at different driving time intervals. The fitting parameters of the curves are listed in Table 2. The changes in used engine oils could be explained by the variations observed in the ratio of CN/C_2. In Fig. 6, the lower CN/C_2 intensity ratio indicated a higher performance of engine oil. The comparison of the ratio of CN/C_2 detected in an oil sample with that of the unused oil could be an indicator of the performance of the engine oil.

All results show that CN and C_2 emissions displayed a unique behavioral variation with increasing driving time intervals. Thus, the evolution of CN and C_2 emissions can be used to evaluate the performance of used engine oils or to diagnose the condition of the motor engine. We suggest to change engine oils when a car's driving time is more than half a year in order to optimize and protect the motor engine.

Conclusions. IA-LIBS was successfully applied to the analysis of the nonmetallic constituents of engine oil. This method was considered as a feasible technique for the evaluation of the consumption and/or combustion of engine oil during routine engine operation. The evolution of CN and C_2 emissions was obtained with different driving time intervals of the motor. It was found that the intensity of CN and C_2 emissions decayed at different driving time intervals. The evolution of total CN and C_2 emissions was plotted, and the CN to C_2 ratio was calculated, which might be taken as an indicator to evaluate the performance of used engine oils and/or to diagnose the condition of the motor engine. All results show that IA-LIBS is a potential technique for determining metallic and nonmetallic constituents of engine oil.

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