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Evaluation of Laser Induced Breakdown Spectroscopy in view of Nickel and Vanadium on line determination in petroleum products

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On line Nickel and Vanadium determination in oils samples was proposed using a Laser Induced Breakdown Spectroscopy to reach low mg/kg concentrations. Both266 nm and 532 nm emissions of a Neodymium YAG laser were evaluated and the visible wavelength gave better results. An original optimization strategy employing a Doelhert design and full quadratic model was carried out. The number of laser shots, the delay time, the integration time gate and the laser energy were selected as factors. Measurements were compared in static and dynamic conditions (i.e. the sample being moved at cc/h flow rate as it is in the process conditions), no significant difference in terms of sensitivity and detection limits was observed due to the viscous nature of the oil samples. Detection limits achieved for vanadium were 7 mg/kg and 31 mg/kg for nickel. In view of on line measurements Czerny turner spectrometer equipped with a photomultiplier was evaluated. Then, the LIBS method developed enabled the plot of linear calibration curves for Ni and V with a sensitivity in agreement with the need of the petroleum industry for on line determination.

Introduction

Metals are occurring in crude oils due to the biogenic formation of oils.[1] Nickel and vanadium, which are the most abundant metallic elements in crude oils, are commonly employed for oil source rock correlation and as tracers of biodegradation.[2] Nickel and vanadium are also well known to affect the cracking conversion process of heavy crude oils and need to be eliminated before hydrodesulfurization. These two metals are responsible for catalyst deactivation, therefore increasing coke formation during the catalytic process. As an example, the presence of metal contaminants in fluid catalytic cracking (FCC) process feeds is known to be a potentially more serious problem. Although sulfur can be converted to gaseous forms that can be readily treated in an FCC unit, the nonvolatile Ni and V contaminants tend to accumulate in the unit during the cracking process and are ultimately deposited on the catalyst together with the coke. Therefore, as poisons of cracking catalysts, these metals are reducing the effectiveness of the whole process.[3-5] Their level is above hundreds of mg/kg in crude oils and should be lowered at tenth of mg/kg in some petroleum products. Therefore, it is essential to be able to quantify the metal content of crude oil but it is also important to follow the metals concentrations throughout the whole process.

A wide range of analytical methods are currently employed for sensitive and accurate determination of metals in oils.[6,7] Most of them are based on laboratory instruments requiring sample preparation or dilution. Atomic absorption spectrometry including flame and flameless systems were described following a mineralization step.[8,9] Two standardized methods based on atomic absorption are now established for the determination of Ni and V in crude oils and residual fuels.[10,11] Some analytical protocols require sample ashing, these are more time consuming; another drawback is vapor phase loss due to the high volatility of some chemical species that cause poor recoveries. The direct procedures involve reduced time, but, in some cases, the composition of the matrix affects the accuracy of the measurements. A minimum preparation, i.e. a simple kerosene, xylene or toluene dilution is possible when using inductively coupled plasmas with optical or mass spectrometric detection (ICP-OES or ICP-MS) [12] and a fair number of standardized methods is existing and based on ICP and direct injection of the petroleum cut.[13,14] In any case, detection limits are substantially degraded relative to aqueous solutions and in some case, the performances in terms of plasma stability are degraded. To prevent signal suppression due to the carbon content of the solvent rich solutions several solutions are described; an optimization of the argon/oxygen ratio to reduce carbon build-up at the interface (ICP-MS cones) but also desolating the solution using an ultrasonic nebulizer (USN).[12] Acid solubilization of the oil achieved in a microwave

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oven exhibits good accuracy and low detection limits (0.02-0.2 µg/g) when analysis is performed using ICP-MS. Nevertheless, the oils must be sampled and the sample digestion requires 30 minutes. Some authors also describe the preparation of emulsions and micro emulsions. The oil is homogeneously dispersed and stabilized as micro droplets in the aqueous phase, which reduces oil viscosity and organic load of the system. Analysis is then performed using ICP.[15-17] Recently Laser ablation coupled to ICP-MS was also described for fast determination of trace elements in lubricating oils [18] or petroleum products including crude oils.[19] Sample is placed in an eppendorf cap and placed in an adapted ablation cell. Low detection limits from 0.005 to 0.008 mg/kg are obtained for V and Ni respectively. Laser ablation is sensitive and requires moderate sample handling but one of the major drawbacks is the lack of accuracy when no calibration standard is available. To overcome this problem, isotope dilution was described by Heilman with a simple mixing of the sample to analyze with enriched solution and further analysis by LA-ID-ICP-MS, a good accuracy was demonstrated by the Ni and V determination in a fuel oil certified material (BCR 164c).[20]

X-Ray fluorescence is also widely employed for metal and sulfur determination in petroleum products [21,22], its sensitivity for metal and sulfur is adequate. Measurement is made on the oil sample without preparation. This obviates any sample dilution, heating or digestion and avoids problems associated with the nebulization. Analyses are possible with minimum support from operators, which facilitates the use of XRF instrument to support a pilot-plant catalyst testing facility.[23] A total-reflection X-ray fluorescence (TXRF) for the determination of S, V, Fe and Ni in crude petroleum oil samples led to low detection limits ranging from 20 mg kg^{-1} for S, 0.6 mg kg^{-1} for V to 0.1 mg kg^{-1} for Fe and 0.4 mg kg^{-1} for Ni. Anyway, with the majority of these methods, the oil must be sampled from the process, brought back to the laboratory and that is time consuming [24] and not in agreement with on-line analysis. To our knowledge, no on line analysis is actually proposed for Ni and V surveys with heavy cuts of petroleum fractions.

Laser induced breakdown spectroscopy is a preparation less method based on the formation of a light emitting plasma onto the sample surface, it has already been employed for determination of metals in solids [25, 26] but also on liquids [27] and petroleum products. [28-30] When compared to laser ablation coupling with either ICP-OES or ICP-MS the main disadvantage is its lower sensitivity, the main advantages are no sampling and fast measurements, leading to a possible on-line measurement.

The aim of this work is to develop a new Laser Induced Breakdown Spectroscopy method in view of building an online instrument for the detection of nickel and vanadium in petroleum products. The targeted concentrations for the two elements are in the low mg kg^{-1} range. Therefore, our focus is the optimization of selected parameters which can influence the sensitivity of LIBS system including the laser pulse characteristics (energy and wavelength), and detection (time resolution parameters) and especially the nature of the spectrometer employed.

Experimental

Materials and methods

The LIBS system employed in this work is a MobiLIBS III purchased from IVEA (France) (fig1). The laser source was a Q-switch Nd-YAG (Brio, Quantel, France) operating at 266 or 532 nm with a fixed repetition rate of 20 Hz and a pulse duration of 4 ns. For the laser operating at 266 nm, the maximum laser energy was 8 mJ/pulse with a fixed spot size of 50 µm corresponding to a maximum 102 GW/cm² irradiance. For the laser operating at 532 nm, the maximum laser energy was 35 mJ/pulse with a 120 µm spot size (i.e.irradiance of 112 GW/cm²). The laser beam was focused onto the liquid surface to a 50 µm spot (266 nm emission) and 130 µm (532 nm). A telescope (design of the MobiLIBS, IVEA, France) was used to image the laser-induced plasma into a fiber connected to the entrance slit of the spectrometer. In this work we have included successively three different spectrometers to the basic design of the MobiLIBS (table 1). The classical Echelle spectrometer (Mechelle 5000, Andor Technology, UK) equipped with an intensified CCD camera (iStar ICCD, Andor Technology, UK). The spectral range was 200 to 980 nm for a simultaneous detection. The LIBS system was controlled by AnaLIBS™ software.

The second spectrometer employed was a Czerny Turner (iHR320, Horiba Jobin-Yvon) also equipped with a iCCD camera from Horiba. The focal distance of the spectrometer is reduced (320 mm) allowing a sensitive detection. The spectrometer was operated using the Labspec^{TM} software from HoribaJobin Yvon. The third spectrometer is a micro-HR, Czerny Turner type monochromator also from Horiba JobinYvon (Courtaboeuf, France) and processed via the AnalibsPM^{TM} software. The micro-HR has a small 10 cm focal length and is equipped with a photomultiplier (PM) detector (Hammamatsu, Japan). Time resolved acquisition is made with a 5 ns interval, the delay time and the integration time gate are selected after measurement and were set from 0 up to 5 µs.

Samples

Samples of feed stream oil, fuel oil and vacuum residue oil were obtained from IFP-EN, their description is provided in table 2.

Sensitivity obtained with the 266 nm laser was poor and led to work using spiked oil samples. An aliquot (10-20 mL) of the oil was mixed with a small volume of organo-metallic solution (Conostan - SCP Sciences, Courtaboeuf, France) with the adapted concentration (Ni, V). The mixture was gently heated and stirred to ensure appropriate mixing. These spiked but diluted oil samples were operated using a flowing liquid configuration described below. Constant renewing of the liquid allowed to perform the complete optimization using the same sample (spiked sample N°6). With the 532 nm emitting laser, sensitivity was improved and it was possible to work directly on the oil samples (non spiked feed stream oil). In view of performing a large number of experiments, the oil was placed in small plastic cups the frozen in order to be solid at room temperature. Prior to a second use of the sample, a second reheating/freezing/analysis/ procedure was applied in order to homogenize the sample. This also allowed to keep a flat and similar sample surface for each experiment. The liquid could be analysed either in a static configuration using with a small oil volume (V<10 mL) or in a flowing liquid configuration (Fig. 1).

With a maximum cinematic viscosity of 22.24 mm²/s measured at 70°C for the feed stream, the oils could also be pumped using tygon tubes (internal diameter=1.02 mm) with a first peristaltic pump (flow rate = 0.6 mL/min) and the flow stream was guided to a small aluminum channel (width = 5 mm). A second peristaltic pump was used to retrieve and transfer the liquid from the channel. This configuration allowed working in closed loop in order to reduce the oil volume required for the analysis.

Optimization strategy

With a laser operating at 266 nm all parameters: number of pulses, fluence, delay time and integration time gate were optimized using a classical univariate approach. For time resolution parameters, the delay time was adjusted while integration time gate was kept constant, and this, until the optimum working conditions are found. The laser energy, the number of laser shots and the number of summed spectra were studied separately and optimized.

At 532 nm, the laser could deliver a significantly higher energy (#35 mJ). A statistical method was selected to study the different parameters available and their interaction. A Doelhert design was selected with four factors. In order to conduct the Doelhert design the experimental parameters to adjust should be identified initially, and the number of levels and factors should also be defined. The number of laser shots, the delay time, integration time gate and the laser energy were the four LIBS parameters selected as factors. These four factors implied a n^2+n+1 experiments, established in five replicates. Randomly, all experiments were carried out using the solidified feed stream oil (table 2). In the design of experiments, the signal-to-noise ratio was selected as the response. The statistical treatment of experimental data was performed using Nemrod™ software.

Results and discussion

Selection of spectral region of interest in the crude oil

Fuel oils are complex mixtures, mainly composed of hydrocarbon (aliphatic and aromatic compounds), sulfur, nitrogen and oxygen compounds, but also metals such as nickel and vanadium. A complex emission spectrum is obtained due to numerous molecular bands (C2 and CN) in the 350 to 570 nm region. To illustrate this, figure 2 shows a feed stream oil spectrum.

The second difficulty is the presence of a significant background between 350 nm and 800 nm. The selection of nickel and vanadium emission lines is important to obtain the best analytical performance (i.e. avoiding spectral interferences and increasing the signal to background ratio and thus the signal to noise ratio). Indeed, the line of interest should not be interfered but also not be self-absorbed and ideally should be relatively isolated in a low background region. Consequently, the region of interest was focused on 300 – 350 nm where the vanadium ionic lines at 309.316 nm, 310.230 nm and 311.071 nm could be isolated and nickel atomic lines at 311.838 nm, 310.187 and 341.476 nm. Among all these lines, the most sensitive and not interfered ones were the V II 309.316 nm and Ni I 341.416 nm.

Selection of laser emission wavelength, energy and detection parameters

Laser operating at 266 nm

The influence of the laser energy on the line intensity and the signal-to-noise ratio (SNR) for nickel and vanadium was studied for 2, 4, 6 and 8 mJ/pulse with a small spot size of 50 µm (corresponding to laser irradiances of 100 GW/cm², at maximum energy). The net intensity represents the intensity sum from three adjacent pixels, and the noise is the standard deviation from 10 pixels intensity selected on the left and right hand sides of each line. The net intensity and the signal-to-noise ratio of Ni I 341.416 nm and V II 309.316 nm follow a linear increase with the laser energy (Fig.3). The best signal and the best signal-to-noise ratio (SNR) were achieved at high laser irradiance. Therefore, a laser energy of 8 mJ/pulse was selected to carry on with the optimization.

As a time resolved signal evolving quickly as a function of time, the laser induced plasma signals of the analytes should be optimized regarding the time resolution parameters: delay time and integration time gate. The delay time represents the delay between laser pulse and beginning of integration time gate, the two parameters were studied in combination. The signal-to-noise ratio of Ni I 341.416 nm line and V II 309.316 nm were plotted as function of the delay time and the integration time gate (Fig. 4). The signal intensity (intensity sum from three adjacent pixels) between 50 ns and 300 ns time delay dropped significantly faster for the ionic vanadium line than for the atomic nickel line, after 300 ns the two lines decreased similarly. Consequence on both signal to noise ratios is a significantly higher value using a 300 ns delay time. The integration time gate was better for elevated values for Ni (fig 4a) while an optimum value of 2 µs was best for the vanadium line (fig 4b). A compromise was selected using a delay time of 300 ns and a integration time gate of 2 µs.

The number of laser shots was then evaluated under optimal conditions. The net intensity and the background for nickel and vanadium increased linearly with the number of laser shots. Elevated values allowed smoothing the noise, increasing therefore the signal to noise values. Best compromise was achieved employing 150 laser shots. To further improve the SNR, while keeping a short analysis time, a sum from 9 and 25 spectra per analysis was tested for each element. For nickel, no difference was observed. However, for the vanadium, the relative deviation of background (RSDb) decreased from 10% to 4% and the signal-to-noise ratio was improved by a factor of approximately 2.5, so 25 spectra were summed for one analysis. Consequently, each analysis represents 25x150 laser shots. The limit of detection (LOD) was estimated according to the expression:

$$LOD = 3\times\sigma\times C\times S^{-1}$$

where σ was calculated from 5 measurements of the background intensity, C was the element of interest' concentration in the sample and S was the emission line signal. [31] Limit of detection were estimated at 50 mg/kg for nickel and at 20 mg/kg for vanadium in the fuel oil samples. These values were close to the target (mg/kg) but still too high and obtained in spiked diluted samples.

Laser operating at 532 nm

Opposite to most samples analyzed by laser-assisted spectroscopy and due to their optical properties, oils may absorb a large spectral range (from UV to IR light). If UV emitting laser are often employed to avoid shielding effect.[32] A laser emission at 266 nm requires additional and well aligned optics, less compatible with on-line measurements. In addition, using the same (Nd:YAG) laser emitting in the visible allowed to work with a plasma with similar irradiance (due to increased spot size) but a larger volume.

In order to optimize simultaneously LIBS parameters with a laser operating at 532 nm, the study was carried out using a Doehlert design and a full quadratic model. The number of laser shots, the delay time, the integration time gate and the laser energy were selected as four factors. Minimum and maximum levels of each factor were chosen according to results from previous experiments (Table 3). Doehlert matrix was composed of 21 experiments and required different number of levels for each factor. In fact, a model with 5, 7, 7 and 3 levels was used for the number of laser shots, the delay time, the integration time gate width and the laser energy, respectively. A number of 7 levels was chosen for the delay time and the gate integration time as the signal is likely to drastically differ for a moderate variation of these parameters.

Following the data processing; the resulting model for SNR is:

$$SNR = 12.59 + 3.38xN - 7.27xD - 1.24xG + 2.00xE - 4.19xN^2 - 2.89xNxD - 6.15xDxG$$

Where N, D, G and E represent the number of laser shots, the delay time, the integration time gate and the laser energy, respectively. Coefficients of model demonstrated that the delay time is the most significant factor on the signal-to-noise ratio of vanadium emission line. The number of laser shots, the integration time gate and the laser energy are also significant factors. In addition, the square term (number of laser shots x number of laser shots) and the interactions (number of laser shots x delay time; delay time x gate width) are also statistically significant.

Two response surfaces are presented in Figures 5 a-b. On the first response surface, the SNR of vanadium line is plotted as a function of the laser energy and the number of laser shots. When the delay time and the gate width are set to the middle of their experimental range, respectively equal to 2550 ns and 5.25 µs. Analysis of the response surface shows that the signal-to-noise ratio of vanadium increases significantly with the laser energy and the number of laser shots. A laser energy of 34 mJ/pulse and a number of 200 laser shots achieved the best SNR. On the second response surface, the SNR of vanadium line was plotted as a function of delay time and gate width in optimal conditions of the laser energy and the number of laser shots selected on the first response surface. The SNR increases with the integration time gate width and it decreases with delay time. Consequently, a signal to noise ratio of 30 was predicted for a short delay time (<500 ns) and a long gate width (>8 µs). The optimal LIBS parameters obtained thanks to the design of experiments were 415 ns for the delay time, 22 µs for the integration time gate, 200 laser shots accumulated for one spectrum and the maximum laser energy.

Following the results of the Doehlert factorial design an experiment was carried out using the predicted optimal conditions, i.e : 22 µs for the gate integration time, 200 laser shots for one spot. The maximum laser energy available at that time: 32 mJ was employed. These predicted optimal parameters, gave experimentally a detection limit of 17 mg/kg. In comparison with the value obtained with the laser emitting at 266 nm (20 mg/kg), the detection limit for vanadium was improved. After the optimization of four first parameters using the Doehlert plan, the number of spectra summed was further evaluated using simple iterative method. A number of 1, 5, 10, 15, 20 and 25 spectra summed were tested. The V II 309.316 nm SNR increased between 1 and 5 summed spectra and remained approximately constant for a value greater than 5. Therefore, it was decided to sum 5 spectra for each measurement corresponding to a total of 1000 laser shots and an analysis time less than 1 min, which is quite suitable for an on line measure.

For Nickel, the sample available contained low concentrations (i.e from 4 to 58 mg/kg). Signal was detected only in the vacuum residue oil, a signal of nickel was detected and a signal to noise ratio of 3 was obtained, it allowed estimating 58 mg/kg limit of detection for nickel which is quite similar to the value obtained with the 266 nm emitting laser.

Study of vanadium and nickel response as a function of sample parameters

In view of LIBS measurements from flowing liquids a study of the Ni and V responses as a function of sample and flow parameters was performed. The viscous petroleum products were pumped via peristaltic pumps into a metallic channel as shown on figure 1. The flow rates employed was small from 0.05 to 2 mL/min to be similar to the process flow employed in a pilot process. The fuel oil flows into a small channel, a fixed focal spot (i.e. fixed vertical position) results in a focal area (size of the spot and focalization degree) depending on the liquid level in the channel. This level may fluctuate with the viscosity of the fuel oil and with a modification of the flow rate, consequently a study of the signal was tested. The “focal point” was placed at the liquid surface and up to 8 mm above the sample surface first in a static mode then in flowing configuration. This “focal point” is pin pointed using the two positioning lasers of the MobiLIBS instrument. Results obtained are presented on figure 6.

Different species occurring from sample N°5 composition (V, Ca, N, C2, CN) and atmosphere (N) are recorded. The nickel signal was not detected. As observed from figure 6, CN and C2 exhibited a higher intensity with focalization onto the sample surface (6 a), whereas calcium and especially vanadium produced increased intensity when focalization was made above the surface (6 b). In this case, no significant effect of the liquid flow could be seen. On the contrary, when the flow rate increased, a 20 % signal drop was observed for vanadium using focalization onto the sample surface (6 a). Both the nitrogen and the carbon lines exhibited a very different behavior with a 60 % intensity difference between focalization (a) and (b).

In order to explain these experiments, an image of the localization of the different emissions would be helpful. In the case of focalization (a), observation in the petroleum flowing liquid are consistent with the study of Motto Ros et al [33], as they performed imaging study of a LIBS plasma produced on a plastic sample the N emission is located close to the sample surface that explains our high N intensity on the figure 6 (a) while C2 and CN emissions are also intense. Focalization above the liquid surface (b) is seldom realized in LIBS analysis as it is likely to produce air breakdown above the liquid surface and therefore an unstable signal. In the case of petroleum sample it produced a high intensity for vanadium and did not degrade signal stability as seen from the error bars. This configuration was selected for further study.

When comparing the previous static liquid configuration to our optimized flowing liquid configuration the vanadium SNR obtained for the fuel oil N° 1 were 17 in flowing and 18 in static liquid configurations. The relative standard deviation of net signal of V II 309.316 nm line, calculated on 25 repetitions of the measure was equal to 18% for the static liquid analysis and 14% for the flowing liquid analysis. No significant difference was observed between static and flowing liquid configurations.

As the LIBS measurement should adapt several petroleum samples, from the quasi-solid vacuum residue to the less viscous fuel oils. Evaluation of the response as a function of the sample nature was achieved using various fuel oils. The samples were provided by IFP-EN with their concentration obtained using X ray fluorescence (table 2). Figure 7 represents a plot of net signal intensity for the most sensitive vanadium line (V II 309.316 nm) as a function of vanadium concentration. Samples employed for the calibration were N°2, 3, 4, 5, 7, 8 and the feed stream oil.

As seen from the regression coefficients linearity is fair when the net signal is plotted. Vanadium signal could be normalized using a CN signal at 419.720 nm to compensate for undesirable variations of the measurement conditions. In this case the linearity is significantly improved with a 0.995 determination coefficient. Despite the different origins and properties of the samples (density and viscosity), a linear calibration could be plotted.

Selecting an adapted spectrometer for on line design

As seen from previous sections, the detection of vanadium is possible in the ten mg/kg range while at the same concentration nickel is still not detected. So, in view of adapting the LIBS system for on-line analysis a more sensitive detection should be employed. Although an echelle spectrometer equipped with an iCCD camera is adapted for simultaneous multielemental detection over a wide spectral range, it requires a severely controlled environment (dust and temperature) which makes it difficult for on line integration in a process hall.

The first adaptation was to select a spectrometer with a shorter focal length to obtain a higher spectral efficiency. A Czerny Turner type spectrometer with a 320 mm focal length and blaze wavelength of 350 nm was tested. The output of the optical fiber was connected to the entrance slit of the spectrometer in order to compare exactly with the above-optimized laser and detection parameters. The vacuum residue oil was analyzed, using the signal to noise calculation detection limits of 7 mg/kg for vanadium and 31 mg/kg for nickel were found. Using this Czerny Turner type spectrometer detection of nickel was significantly improved. This experiment showed that a more efficient Czerny Turner spectrometer should be employed to fit better with the detection limit target values.

To go further with the adaptation for on line analysis, a second Czerny Turner spectrometer equipped with a photomultiplier (PM) was tested. The photomultiplier detection offers the advantage of reduced size a good sensitivity. In this view, an even more compact system was selected (microHR) with a focal length of 10 cm. As in the previous experiment, the laser head and light collection system were kept from previous optimization. Nevertheless, the detection parameters were not the same due to the PM specifications. Signal on a single channel is recorder with a five ns step. Signal is summed over a 12.5 µs period and no background subtraction was possible. It was also necessary to use a lower laser energy: 12 mJ to avoid a saturation of the photomultiplier. The samples N° 6, 9, the feed stream and the vacuum residue oils were analyzed. Signal as a function of concentration is plotted for nickel using Ni 341.316nm emission line (figure 8). Nickel concentration is ranging from 5 to 58 mg/kg, the maximum relative standard deviation of nickel signal based on 20 measurements was equal to 4.6%. For Vanadium, sample concentrations are ranging from 9 mg/kg to 183 mg/kg with a maximum RSDs of 3.5 %. As no blank sample could be found the LOD was difficult to compare with the Mechelle system, nevertheless as it can be seen from fig 8 a linear response was obtained for both elements with R^2 coefficient superior to 0.998.

Compared to the previous LIBS system (Mechelle spectrometer coupled with an ICCD camera), detection of nickel was significantly improved allowing to detect the lowest nickel concentrations: 5 and 13 mg/kg with RSDs in the 5% range. Vanadium was less sensitive than Nickel, as shown by the calibration curve slope, nevertheless here also the lowest concentration: 9 mg/kg could be detected with a RSDs of 3 %. These results were promising in view of building an on line system for Nickel and Vanadium determination.

Conclusions

In order to integrate a LIBS system on industrial processes for on line analysis, different LIBS parameters were evaluated for the analysis of nickel and vanadium in crude oil samples. LIBS parameters, including laser wavelength, were selected to obtain best sensitivity and detection limits. Effect of the sample flow rate was also evaluated by comparison of a static liquid and flowing liquid configurations. The results showed no significant differences in terms of limits of detection between these two analytical configurations

Best results were obtained using a 532 nm emitting laser. The use of a design of experiments allowed to quickly optimize LIBS parameters: laser pulse energy, delay and integration time gate. Using the predicted parameters the detection limits were in the 10 mg/kg range for vanadium and still above 50 mg/kg for nickel. Vanadium response was found to be linear over a 10 to 70 mg/kg concentration range. The study of focalization and a careful selection of a Czerny Turner type spectrometer equipped with an iCCD camera allowed to lower the detection limit to 7 mg/kg for vanadium and 31 mg/kg for nickel. It was further demonstrated that the use of a more compact Czerny Turner spectrometer (microHR) coupled to a photomultiplier was sensitive enough to observe a variation of LIBS signal between the lower concentrations of both nickel and vanadium of interest (in the 5-50 mg/kg). No detection limit was calculated due to the lack of blank sample.

Our results exhibited that a moderate flow rate as it is employed in a pilot-plant will have no significant effect on LIBS measurements. The liquid can flow in a channel directly using the liquid flow rate of the process. Minor variations of the pilot flow rate had no significant impact on element response. On line analysis can be achieved using a visible laser, a compact spectrometer equipped with a photomultiplier with the use of a LIBS cell for liquid analysis.[34]

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References

1 A. J. G. Barwise, *Energy Fuels,* 1990; 4: 647.
2 M. D. Lewan, *Geochim. Cosmochim. Acta*, 1984; **48**, 2231.
3 P. I. Premovic, D. M. Dordevic, M. S. Pavlovic, *Fuel*, 2002; **81,** 2009
4 S. Lo Monaco, L. Lopez, H. Rojas, D. Garcia, P. Premovic, H. Briceno, *Organic Geochemistry*, 2002; **33**, 1593.
5 K. Taegon, R. Jaewook, K. Min-Ji, K. Hyun-Jong, S. Yong-Gun, J. Yukwon, P. Joo-Il, *Fuel*, 2014, **117**, 783.
6 C. Duyck, N. Miekeley, C. L. Porto da Silveira, R. Q. Aucélio, R. C. Campos, P. Grinberg, G. P. Brandão, *Spectrochim. Acta B*, 2007, **62**, 939
7 R. Sanchez, J.L. Todolí, C.P. Lienemann, J.M. Mermet, *Spectrochim. Acta B*, 2013, **88**, 104.
8 R. Q. Aucelio, A. Doyle, B S. Pizzorno, M S. Tristao, R. C. Campos, *Microchem. J.*, 2004; **78**, 21.
9 M. Bettinelli, P. Tittarelli*, J. Anal. At. Spectrom,* 1994, **9**: 805.
10 ASTM D5863. Standard Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry. http://www.astm.org. 2011.
11 EN 13131. Liquid petroleum products - Determination of nickel and vanadium content - Atomic absorption spectrometric method.
12 C. Duyck, N. Miekeley, C. L. P Silveira, P. Szatmari, *Spectrochim. Acta B* , 2002; **57**, 1979.
13 ASTM D5708 – 12,) Standard Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry.http://www.astm.org. 2012.
14 ASTM D7691 –11 Standard Test Method for Multielement Analysis of Crude Oils Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). http://www.astm.org. 2011.
15 M. P. Escobar, B. W. Smith, J. D. Winefordner, *Anal. Chim. Acta,* 1996; **320**, 11.
16 R. M. De Souza Roseli, A. L. Scarminio, C. Duyck, C. L. P. Da Silveira, R. Q. Aucelio, *Microkimical Journal,* 2007, **87**, 99.
17 R. E. Santelli, E. Padua Oliveira, M. Batista de Carvalho, M. Almeida Bezerra, A. SoaresFreire, *Spectrochim. Acta Part B* 2008, **63**, 800.
18 N. H. Bings*, J. Anal. At. Spectrom,* 2002; **17**, 759.
19 E. Ricard, C. Pécheyran, G. Sanabria Ortega, A. Prinzhofer, O. F. X. Donard, *Anal Bioanal Chem*, 2011, **399**, 2153.
20 J. Heilmann, S. F. Boulyga, K. G. Heumann, *J. Anal. At. Spectrom*, 2009, **24**, 385.
21 ASTM D6376 – 10 Standard Test Method for Determination of Trace Metals in Petroleum Coke by Wavelength Dispersive X-ray Fluorescence Spectroscopy. http://www.astm.org. 2010.
22 ISO 14597 –Petroleum products -- Determination of vanadium and nickel content -- Wavelength-dispersive X-ray fluorescence spectrometry. http://www.iso.org. 1997.
23 E. R. Denoyer, L. A. Siegel, *Anal. Chim. Acta,* 1987, **192**, 361.
24 N. Ojeda, E. D. Greaves, J. Alvarado, L. Sajobohus, *Spectrochim. acta part B*, 1993, **48**, 247.
25 A. Stankova, N. Gilon, L. Dutruch, V. Kanicky, *Fuel*, 2010, **11**, 3468.
26 B. Bousquet, J-B. Sirven, L. Canioni, *Spectrochim. acta part B*, 2006, **62**, 1582.
27 F-A. Barreda, F. Trichard, S. Barbier, N. Gilon, L. Saint-Jalmes, *Anal. Bioanal. Chem*., 2012, **403**, 2601.
28 M. A. Gondal, T. Hussain, Z. H. Yamani, M. A. Baig, *Talanta* 2006, **69**, 1072.
29 M. A. Gondal, M. N. Siddiqui, M. M. Nasr, *Energy & Fuels* 2010, **24**, 1099.

30 J. L. Tarazona, J. Guerrero, R. Cabanzo, E. Mejia-Ospino, *Applied Optics,* 2012; **51**, B108.

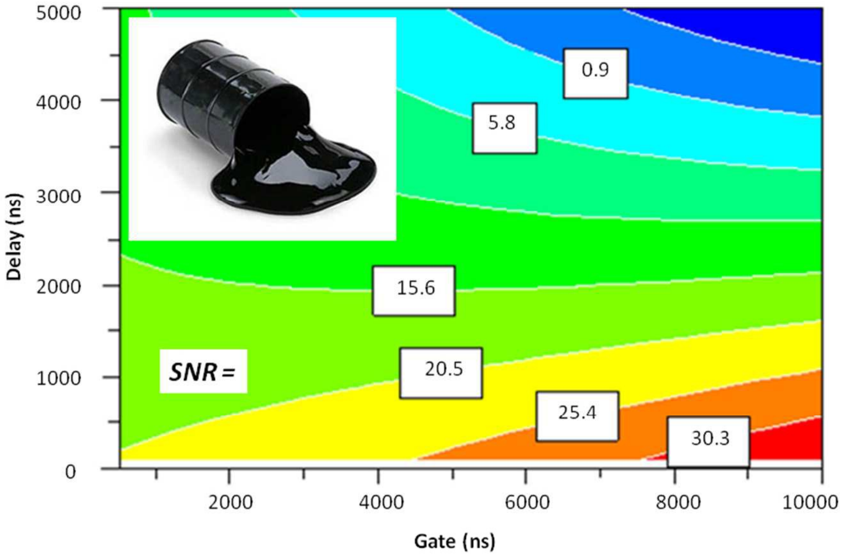
31 C. L. A. URRIE, *Pure&Appl. Chem*, 1995, **67,** 1699.

32 J. A. Aguilera, C. Aragon, F. Penalba, *Applied surf. sci.,* 1998, **127,** 309.

33 V. Motto-Ros, QL. Ma, S. Grégoire, W.Q. Lei, XC. Wang, F. Pelascini, F. Surma, V. Detalle, J. Yu, *Spectrochim Acta Part B,* 2012, **74–75**, 11.

34 Patent N°14/53.735, Système de mesure de la composition d'un liquide par spectroscopie sur plasma induit par laser, april 2014

Laser induced breakdown spectroscopy (LIBS) has been evaluated for the purpose of analyzing petroleum products. Optimization in view of an on line LIBS control is presented.



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	Spectral Range(nm)	**Focal length (mm)**	**Spectral resolution (pm) at 230 nm**	**Detection**
Mechelle 5000	200-980	-	100	iCCD
iHR 320	150-850	320	60	iCCD
MicroHR	180 - 500	140	100	PM

Table 1: Spectrometers specifications.

Sample	[Ni] mg/kg	[V] mg/kg	density d (15°)	Kinematic viscosity at 100°C (cSt)	Description
Feedstream oil	22	68	n*	n	Compound of paraffins, naphtenes, aromatics and asphaltenes (87% C; 14% H, 2% N; 1,5% O and <0,1% metals)
Vacuum residue oil	58	183	n	n	Residue of the crude oil distillation compound of saturated, aromatics, resins and asphaltenes
Fuel oil N°1	34	96	0.9223	16	Fraction obtained from the crude oil distillation compound of naphtenes (85%), aromatics (10%) and olefins (1%)
Fuel oil N°2	42.90	10.30	n	n	*description identical to fuel oil N°1*
Fuel oil N°3	20.80	61.60	n	n	*description identical to fuel oil N°1*
Fuel oil N°4	20.20	31.80	n	n	*description identical to fuel oil N°1*
Fuel oil N°5	22.70	72.00	n	n	*description identical to fuel oil N°1*
Fuel oil N°6	4.18	7.97	0.9565	148	*description identical to fuel oil N°1*
Fuel oil N°7	8.20	15.20	0.9720	100	*description identical to fuel oil N°1*
Fuel oil N°8	22.30	45.80	n	n	*description identical to fuel oil N°1*
Fuel oil N°9	24.70	13.60	n	n	*description identical to fuel oil N°1*

**n = data not available.*

Table 2: Description and elemental composition of oil samples

Variable	LIBS parameter	(-)	(+)
X1	Number of laser shots	20	250
X2	Delay time (ns)	100	5000
X3	Gate integration time (µs)	0.5	10
X4	Laser energy (mJ/pulse)	20	35

Table 3: Factors and levels used in Doelhert design

Fig. 1: LIBS system employed. Two setups for viscous liquid analysis: **a** flowing liquid analysis in an aluminum channel and **b** static liquid analysis.

Fig. 2 Feedstream oil spectra: **(a)** 300-400 nm with a zoon on the region of interest for Ni and V detection; **(b)** 400-480 nm and **(c)** 480-580 nm. Instrument is a conventional MobiLIBS III, Laser: 532 nm, energy: 32 mJ, delay time: 415 ns, integration time gate: 22 µs.

Fig.3: Line intensity and SNR of Ni I 341.416 nm and V II 309.316 nm as a function of laser energy. The results were carried out in flowing liquid configuration with a delay time of 700 ns, an integration time gate width of 2 µs and a number of 100 laser shots. Sample was N°6 (table 2) spiked at 1200 mg/kg Ni and V metalo-organic standards.

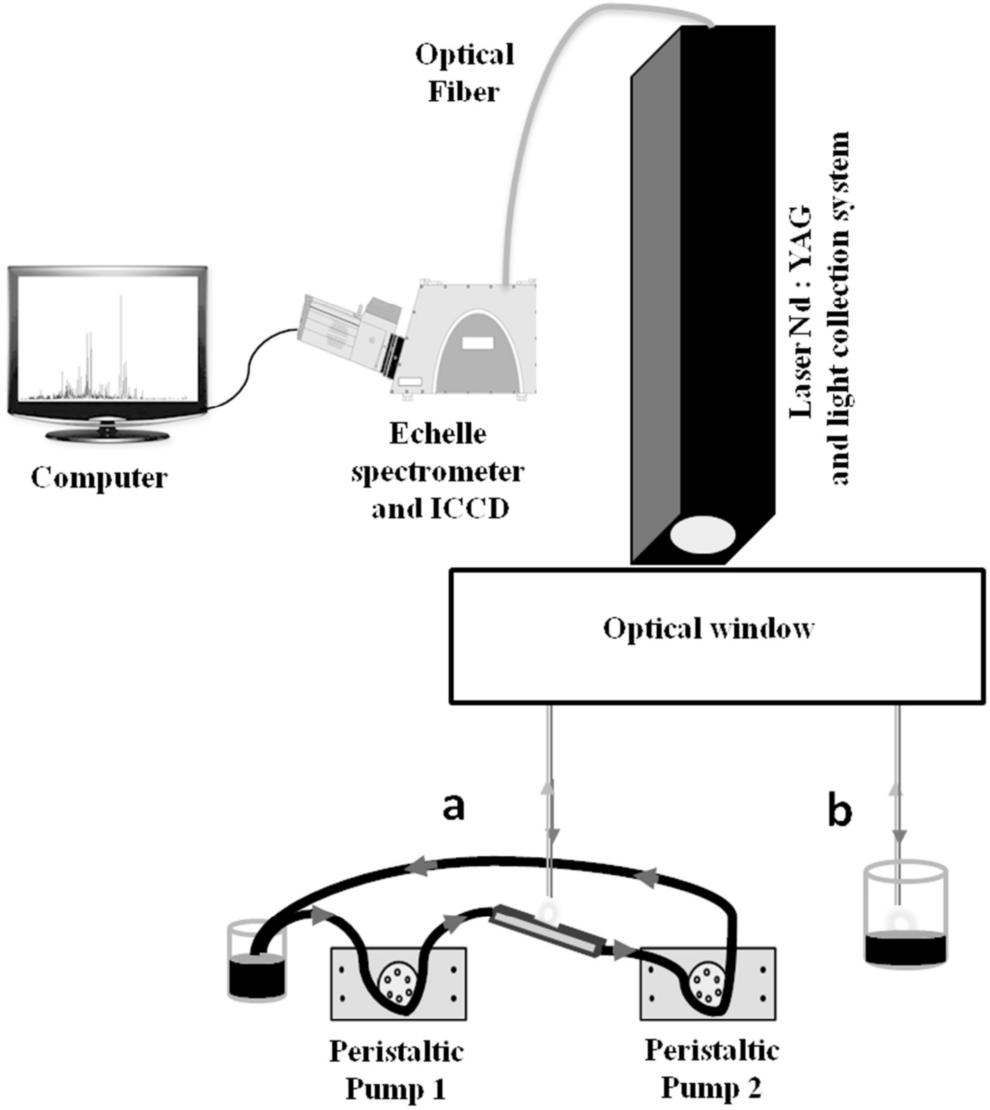
Fig.4: The SNR of Ni 341.416 nm and the background emission as a function of delay time and integration time gate. The results were carried out in flowing liquid configuration with a laser energy of 8 mJ/pulse and a number of 100 laser shots. Sample similar to fig 3 is employed.

Fig.5: 2D representation of the response surfaces obtained on the feed stream oil (table 2) analysed in static liquid configuration. **a** : SNR as function of the laser energy and the number of laser shots with a delay time of 2.55 µs and an integration time gate of 5.25 µs and **b**: SNR as function of the delay time and the gate integration time with a laser energy of 34 mJ/pulse and a number of 200 laser shots.

Fig. 6: Signal intensity (normalized to highest value), as a function of liquid flow rate in the channel. Focal point (a) refers to the sample surface while (b) refers to 8 mm above the liquid surface. Measurement conditions are similar to fig 5b, delay 415 ns integration time gate 22 µs. Sample N°5 is employed.

Fig. 7: Calibration curves obtained for vanadium using optimized conditions: laser energy 32 mJ, 200 laser shots accumulated, delay 415 ns integration time gate 22 µs. Net signal for vanadium at 309.316 nm (orange circle) and vanadium signal normalized to CN, i.e. V I 309.316 nm to CN 419.720 nm ratio (blue square).

Fig. 8: Photomultiplier signal as a function of increasing V and Ni concentrations, recorded at 309.316 nm for vanadium (orange circle) and 341.416 nm for nickel (green diamond).



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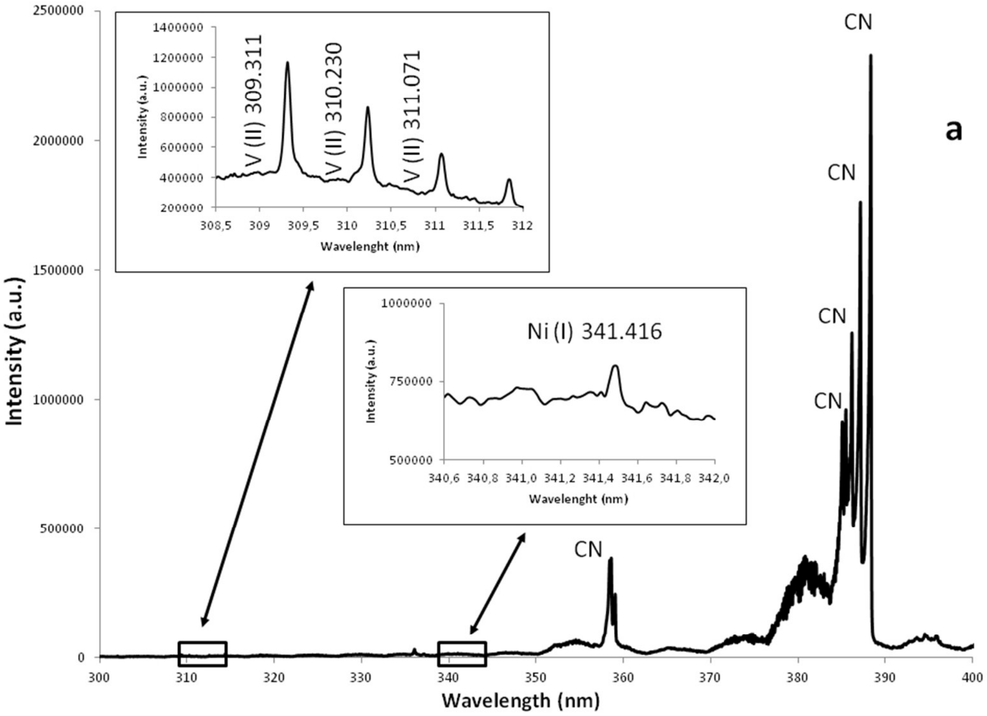

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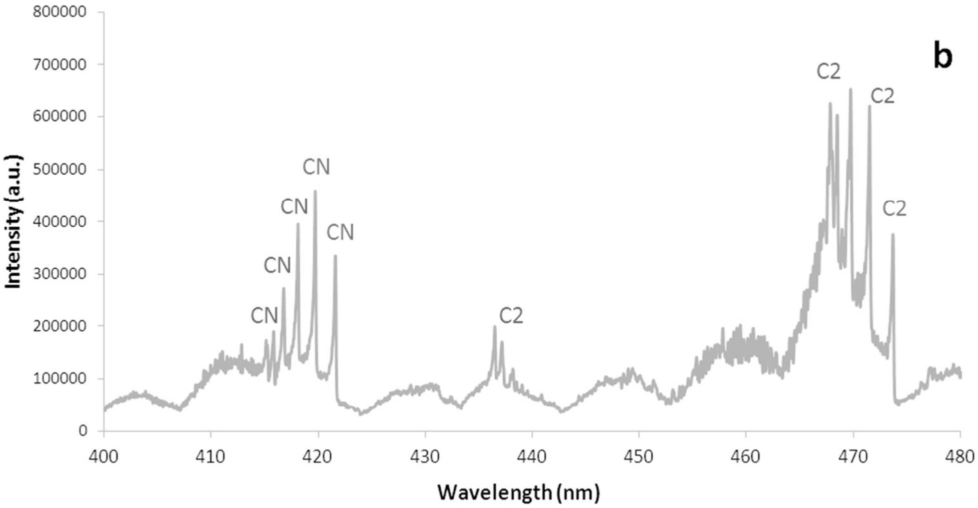

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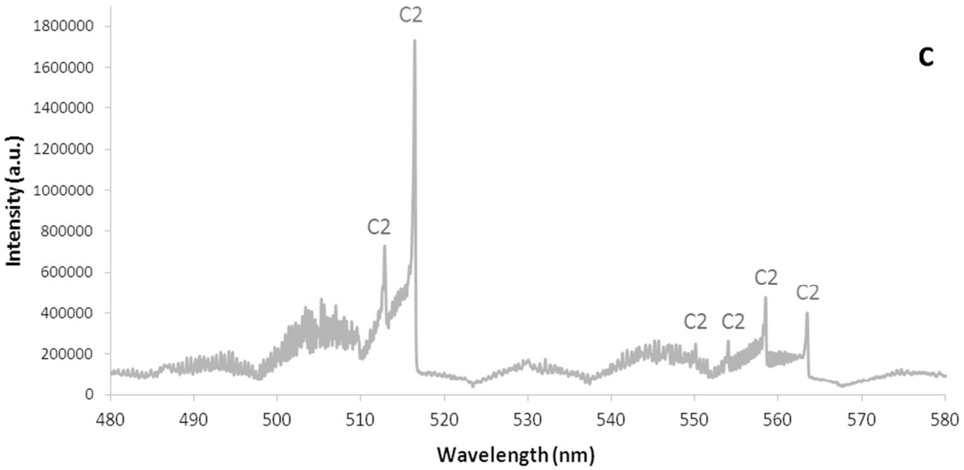

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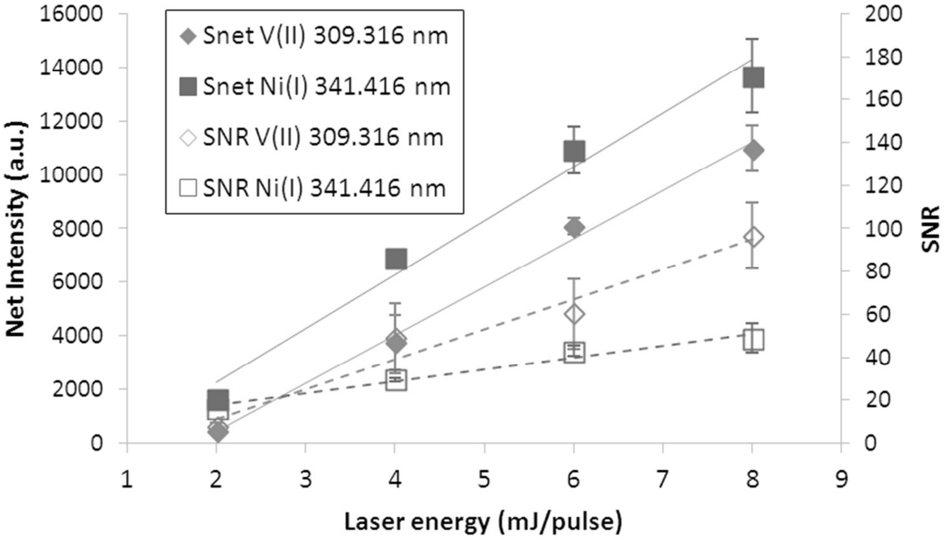

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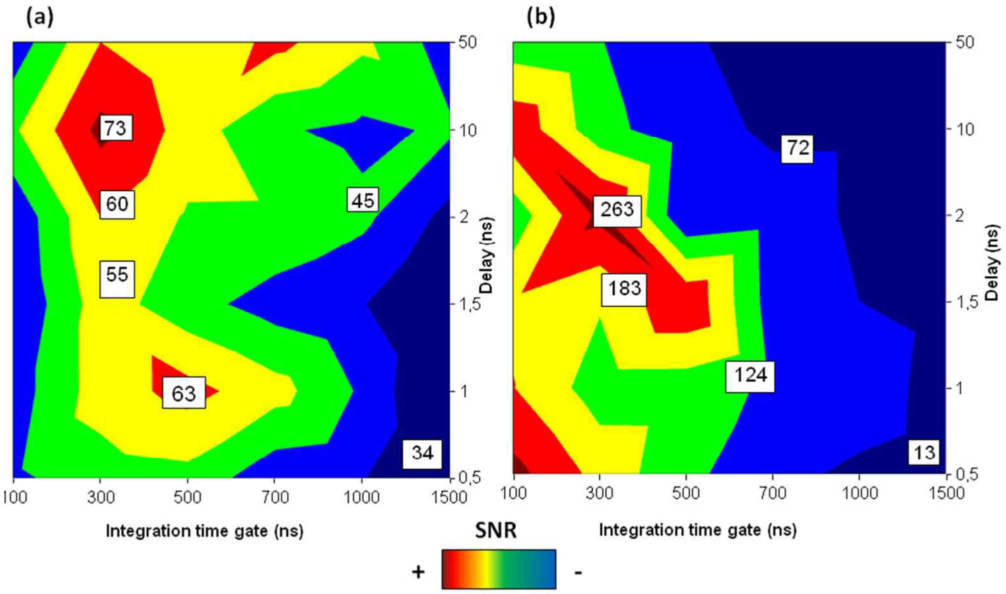

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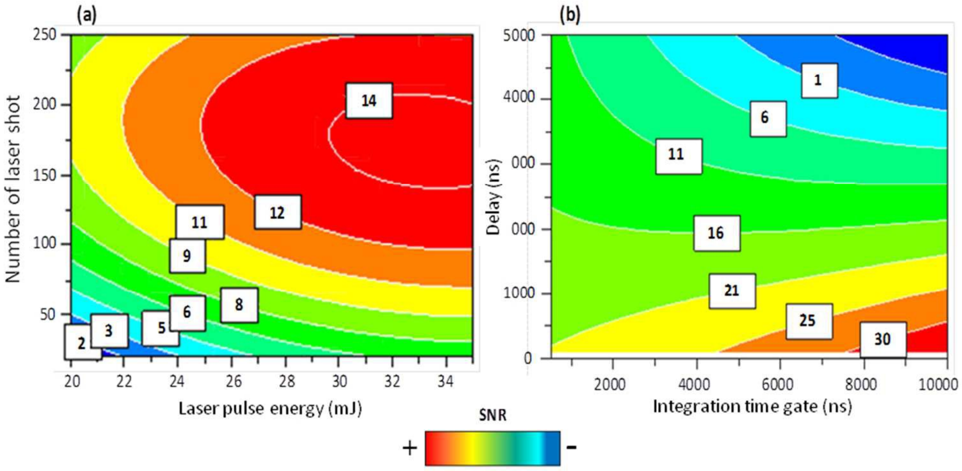

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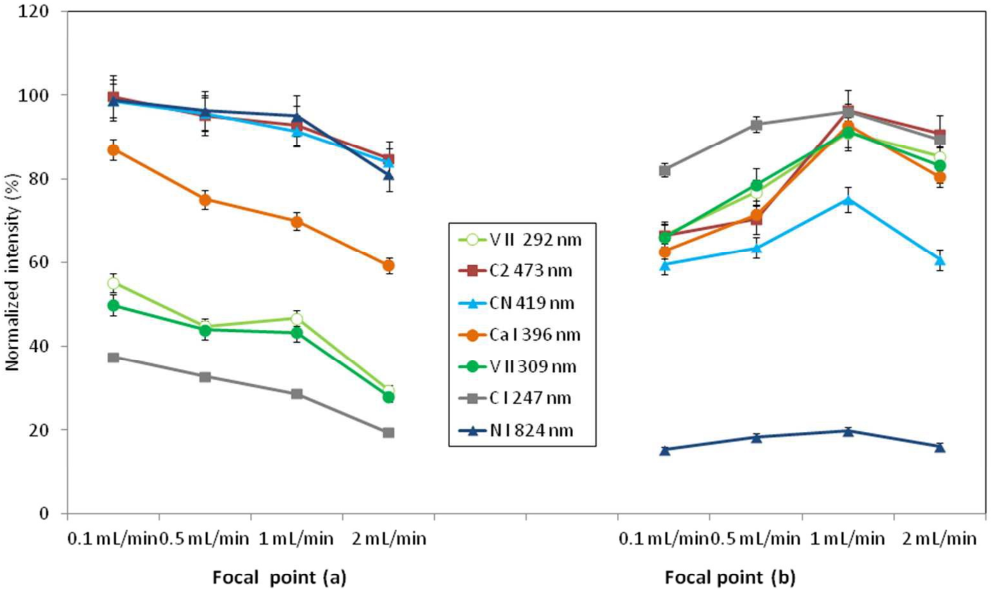

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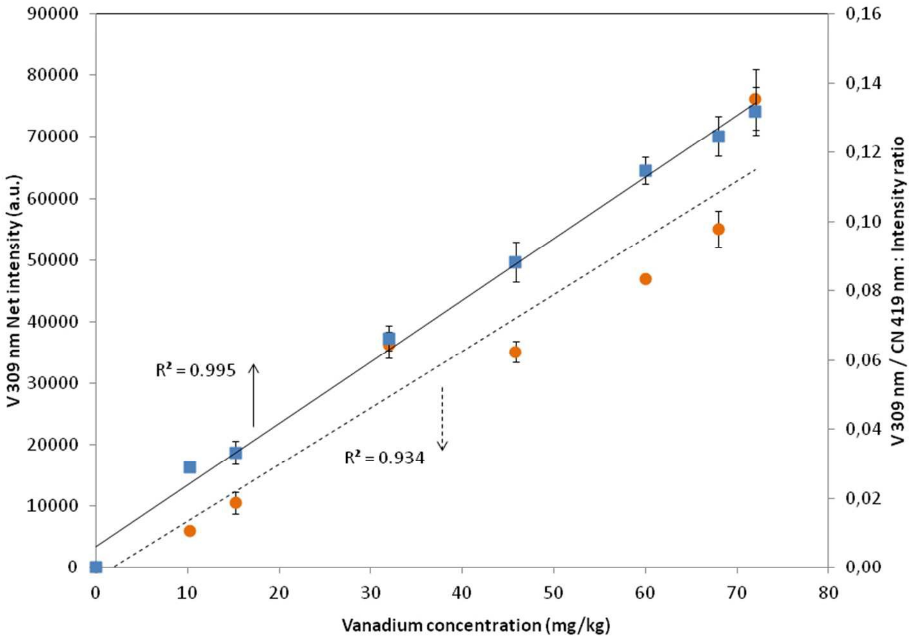

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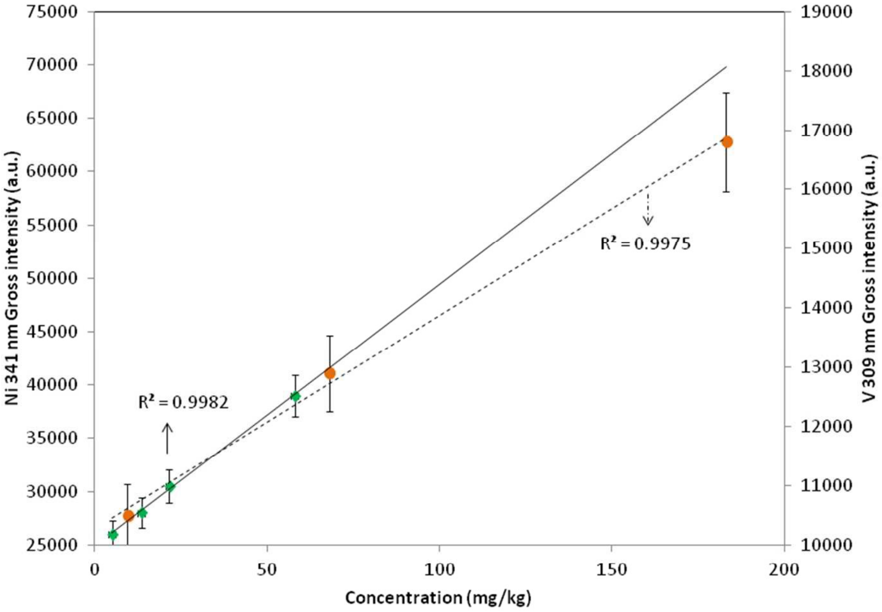

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