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Application of spatial confinement for gas analysis using laser-induced breakdown spectroscopy to improve signal stability

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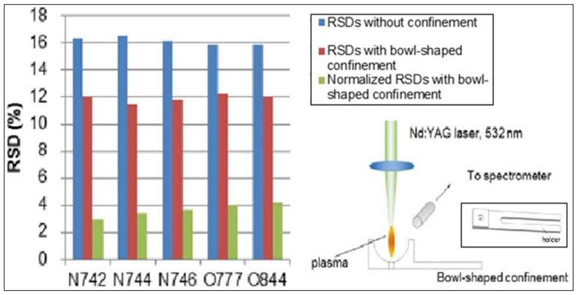
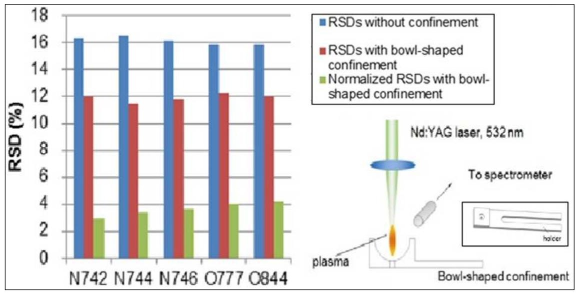


Bowl-shaped confinement was designed to increase signal stability for gas analysis using LIBS.



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The quantitative analysis of gaseous samples using laser induced breakdown spectroscopy (LIBS) is even more limited due to its relatively lower signal reproducibility compared with that of solid samples. In this study, a cylindrical spatial confinement was first applied to reduce the signal fluctuations in the analysis of ambient air using LIBS. With the aid of plasma image analysis, bowl-shaped confinements were further designed to reduce the signal fluctuations. The location and the size of the confinement were also optimized to achieve its best effect. Results show that the cylindrical confinement reduces the signal fluctuations to some extent. Compared with using the cylindrical confinement, the shape and position of the plasma are more stabilized and spectral fluctuations are further reduced by using the bowl-shaped confinement. Simply using the traditional spectral area normalization method to alleviate the influence of the variance in plasma energy, the pulse-to-pulse relative standard deviation (RSD) can be reduced to 2.94% for nitrogen and 3.97% for oxygen, which is comparable to the analysis of solid samples.

1 Introduction

Laser induced breakdown spectroscopy (LIBS), as an atomic emission spectroscopy (AES) technology, has been regarded as a versatile analytical technique for gases, liquids, and solids.[1] Several researchers have been conducted on gas analysis using LIBS with the main focus on improving the limit of detection.[2-7] Contrast with its application on solid samples, the analysis of gaseous samples is very limited, mainly limited by its poor measurement precision due to pulse-to-pulse signal variations.[8] Large signal fluctuations also hinder the improvement of the limit of detection (LOD) of elemental analysis, which is also one of the challenges for LIBS applications.[9] For example, even using results derived from the average or the sum of multiple spectra, reported RSDs for gas-phase LIBS analysis are 3.6% for carbon dioxide[10], 7% for sulfur[11], and 8% for chlorine and fluorine[12]. The RSDs of the pulse-to-pulse analysis would be even much higher. For instance, Xu and Majidi reported a pulse-to-pulse RSD of 60% for nitrogen in air.[13]

From literature, the reasons why the spectral signals collected from laser-induced plasma generated from gaseous samples show stronger fluctuations than those from solid surfaces can be mainly summarized as: 1) Instability comes from inevitable floating particles in the gas, which greatly affect the position of the generated plasma from experiment to experiment since the plasma will be mostly initiated from them. It is regarded that the existing of aerosols in ambient air can contribute 60% of the signal fluctuations from pulse to pulse.[14] 2) Another source of instability is the difference in laser energy absorbed by the plasma. Plasma generation needs the multi-photon ionization (MPI) process to provide initial electrons to trigger the avalanche breakdown. Since more photons are required for MPI to happen in gaseous samples compared with solid and liquid samples, the plasma generation in gaseous samples is more likely to be a sporadic event.[15] Uncertainty of initiation time further leads to changes in the proportion of laser energy absorbed by the plasma, causing signal fluctuations.[16] 3) Moreover, the shape of plasma in gas also shows great variations, sometimes with two discrete cores. For the laser pulse energy has a Gaussian profile, the leading edge of the ns pulse will have sufficient irradiance to create the plasma before the peak of the pulse arrives. Then, the remainder of laser energy will interact with the existing plasma and accompanied shockwaves. Due to this interaction, the plasma shape becomes more irregular and even two cores can show up.[17] Since the energy absorbed by the plasma varies from pulse to pulse, its shape may also show great differences. For these reasons, compared with those generated on solid surfaces, the plasma generated in gaseous samples tends to present more fluctuations in its sizes, shapes and positions, which leads to larger signal instability. In addition, since gas molecules are more likely to be pushed to the periphery of the plasma volume according to the plasma-analyte interaction mechanism discussed in Ref. 18, the signal stability will be greatly influenced by the plasma morphology. This mechanism further influences the aerosol-affected gas analysis by introducing shot-to-shot variations into the subsequent emission collection process.[19] Therefore, methods to regularize the plasma itself should be employed during the analysis process to improve the precision of gas analysis by LIBS.

It should be noted that although variations in the plasma morphology and plasma energy influence the signal intensity greatly as we summarized before, other factors can also contribute to the signal fluctuations. These factors include nonlinear laser–material interactions, noises associated with the detection process, and so on. Appropriate statistical methods like the spectra averaging method and the standard deviation approach can be used to eliminate these influences. For more details, one can refer to Ref. 16-21 and other related literatures. Despite using these statistical methods, experimental methods to achieve high signal stability during gas analysis include using fs-laser,[22] filtering aerosols and using a seeding laser,[14] using metal substrate to provide initial electrons[10] and so on.

Confinement has been found to be capable of improving signal quality in our previous work[23-25]. The confinement will increase the precision of measurement in two ways: 1) by stabilizing the shape and position of the plasma; 2) by increasing the plasma's parameters such as electron density and plasma temperature into a range in which the line intensity is less sensitive to the variation of plasma temperature and electron number density[24]. Moreover, for gaseous samples, the reflected shockwave due to the confinement will not only regularize the plasma morphology but also push the generated plasma to the center of the confinement in case the plasma was initiated off-center due to the existence of the floating particles. Stronger line intensity and lower fluctuations will also decrease the LOD. In this work, we first applied cylindrical confinement to stabilize the plasma and reduce the signal fluctuations. Then with aid of information from plasma images, the shape of the confinement was re-designed into bowl-shaped and the size and the location of the bowl-shaped confinement were also optimized. In addition, the application of the confinement is very simple just by fixing the confinement at the position with a certain distance to the focal lens.

2 Experimental setup

The experimental setup used in this study is shown in Fig. 1(a). A Spectrolaser 4000 LIBS system (XRF, Australia) was used for ablation and spectral collection, as described in Ref. 23. In this system, the laser source for plasma producing is a Q-switched Nd:YAG laser with a wavelength of 532 nm. The pulse repetition rate was set at 1 Hz, avoiding interactions between shockwaves from different pulses. The light emitted from the plasma was collected from an angle of 45 degree using a fiber with a lens of 1.25 cm diameter and 2 cm focal length. Then the spectra were detected using four Czerny–Turner spectrometers and CCD detectors, covering a spectral range from 190 to 940 nm with a nominal resolution of about 0.1 nm. The gate width and delay time were 1 ms and 0.7 μs. For plasma morphology, we used an ICCD camera (Andor, iStar 334T) to capture images from 60 degree with the laser beam. The delay time and gate width of the ICCD were set as same as that of the spectrometer to find out the effect of the confinement on signal intensity and stability.

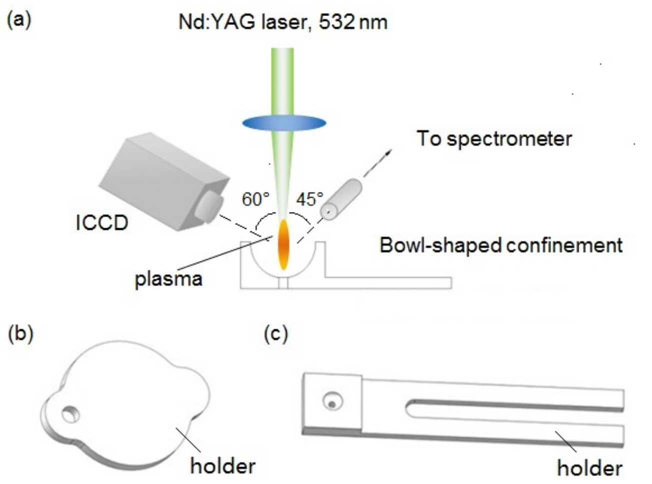

Fig. 1 Schematic diagram of (a) the experimental setup, (b) cylindrical confinement, and (c) bowl-shaped confinement.

The sample used in this work was simply the surrounding air in the clean laboratory of 10K class, which means the number of aerosol particles larger than 0.5 μm in diameter is less than 350 per liter of air. At this level of aerosol concentration, laser-induced plasmas can still be affected by floating particles as described before. We chose three characteristic spectral lines of nitrogen (N I 742.364 nm, N I 744.229 nm and N I 746.831 nm) and two characteristic spectral lines of oxygen (O I 777.417 nm and O I 844.676 nm) for analysis. For the confinement, we used a cylindrical confinement (3 mm in height and 4 mm in diameter) and bowl-shaped confinements with radius of 5 mm, 4 mm and 3 mm, as shown in Fig. 1(b) and (c). The height of bowl-shaped confinements is 5 mm. At the bottom of the hemispherical dome, we drilled a hole with diameter of 2 mm to let the laser pass through. All of them were made of polytetrafluoroethylene (PTFE) plates. The holder of the confinement was fixed onto a XYZ translation stage to facilitate adjusting of its position. For each case, we adjusted the position of the confinements to make the plasma just in the center, avoiding the contact between the plasma and the confinement.

During our experiments, we kept the laser energy at 90 mJ and the spectrometer delay at 0.7 μs. These two parameters were optimized so that we could get clear spectral lines of nitrogen and oxygen from the air plasma. Then we got 50 spectra from each case to calculate the pulse-to-pulse RSD of the signal.

3 Results and discussion

3.1 Results from cylindrical confinement and design of bowl-shaped confinements

At first, the same cylindrical confinement in our previous work[23-25] was applied to stabilize the plasma morphology. The results show that the pulse-to-pulse RSD can be reduced to some extent (as shown by the blue and green bars in Fig. 2). In this work, pulse-to-pulse RSDs are calculated based on the line signal peak intensity, which is the background-subtracted peak area for each spectral line.

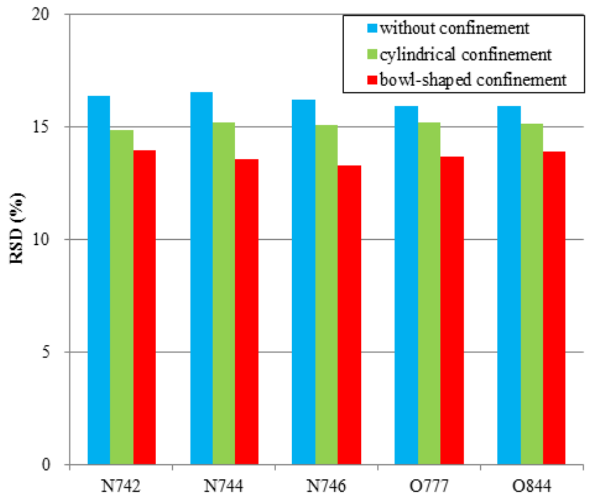

Fig. 2 Pulse-to-pulse RSDs using different shaped confinements.

As suggested in Ref. 24, confinements influence the plasma by reflecting the accompanied shockwave to reheat the plasma and regularize its shape. In case of solid analysis, the laser ablation always happens on the solid sample surface, and the position of the plasma is almost determined due to the confinement of solid surface. Fluctuations mainly come from the variation in the plasma morphology; therefore, the plasma can be more axisymmetric as shown in Ref. 24 when the cylindrical confinement is applied. If the plasma deviates away from its axis, the shockwave on this side will be reflected back into the plasma core earlier than the other side, stabilizing the plasma position and regularizing its shape. However, for the application for LIBS on gas analysis, the fluctuations of signal may also come from its variations along the symmetric axis (laser direction), as pointed out by Ref. 19. Along this direction, the shockwave reflected from the cylindrical confinement has little effect on re-shaping and stabilizing the plasma.

Plasma images taken by the ICCD camera are shown in Fig. 3. In our work, these plasma images were taken without confinement to study the plasma morphology. The gate delay and width were set the same as the spectrometers of our Spectrolaser 4000 LIBS system. In this way, we can see changes in the plasma morphology during the signal collection from pulse to pulse. We can see that plasmas induced by the ns laser in gaseous sample are usually in spheroid shape and present great asymmetry along the axis direction, sometimes even with two cores.

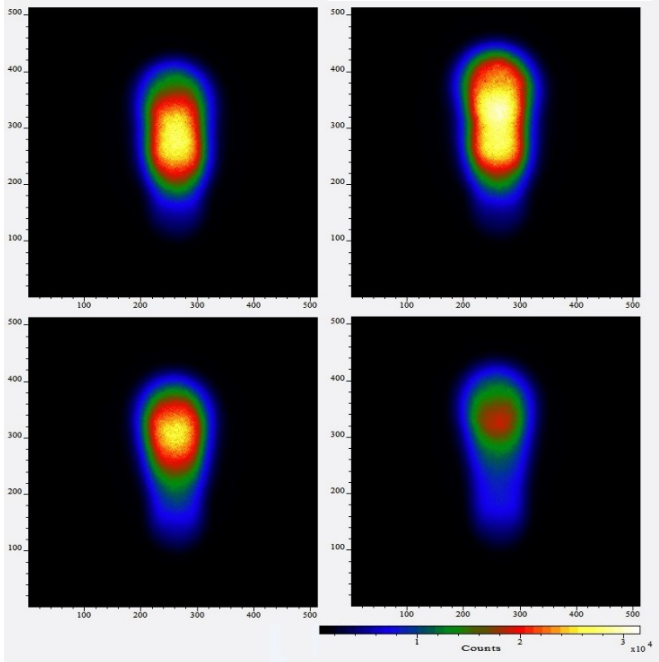

Fig. 3 Typical plasma images without confinement from different pulses under same experimental conditions taken by the ICCD carema from 60 degree with the laser beam, with the gate width of 1 ms and the delay time of 0.7 μs (the size of the plasma is about 5 mm in length).

Observation of plasma images also gives us the following hints: 1) it confirms us the reasons why plasma generated in gaseous samples show great fluctuations, as we summarized before. The plasmas generated from pulse to pulse show great differences in their shapes, sizes and positions. 2) the spheroid shape indicates that the accompanying shockwave around the plasma would rather be an approximately spherical one. 3) the upper part of the plasma appears to be the more steady part, thus it's better for us to reflect the energy from the bottom part of the plasma back into its core. In this way, the plasma's position can be stabilized and its energy can be more concentrated.

Based on these observations, we re-designed the confinement into bowl-shaped as described in the experimental setup, expecting better confining effect on plasmas. Different from the cylindrical confinement, bowl-shaped ones make the energy of the plasma generated in gaseous samples more restricted around its core. It can also reflect the plasma's energy from the bottom to stabilize its axial position. This means the lower the plasma is, stronger shockwave will be reflected to push it back to a higher position, therefore hold the plasma to a relative fixed position. What's more, the reflected shockwave can also converge the molecules outside the periphery back into the plasma center, therefore enhancing the signal intensity and eliminating the influence of plasma morphology on signal stability to some extent. Since the plasma should be generated in the center of the confinement, a hole had to be drilled on the bottom for the laser to pass through and avoid the generation of plasma from the solid confinement material.

By utilizing the bowl-shaped confinement to stabilize the plasma, we can see that the bowl-shaped confinement did impose a greater stabilizing effect on the LIBS spectral signals from the comparison shown in Fig. 2. Furthermore, a stronger signal enhancing effect can also be found in the case of bowl-shaped confinement, as shown in Fig. 4. Line intensity is defined as the background-subtracted peak area for each spectral line using the same data set as in Fig. 2. From line intensities normalized by cases without confinement, we can see the bowl-shaped confinement improved the line intensities by about 50%. This result is in accordance with other researchers who used various confinements as a signal enhancement technology.[26-28]

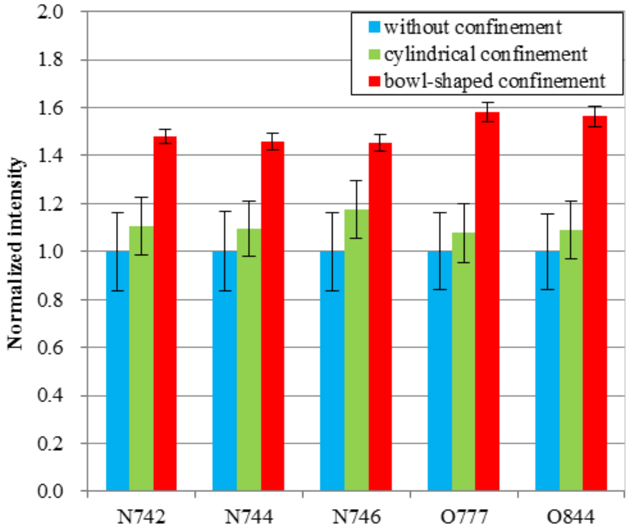

Fig. 4 Averaged initial intensity using different shaped confinements, normalized by the case without confinement.

3.2 Optimization of the position and size of the bowl-shaped confinement

Since bowl-shaped confinements are designed to stabilize the plasma's axial position and re-shape it to be more regular, the axial position is apparently a key parameter of confinement geometry. To find out its influence, we used a bowl-shaped confinement with 4 mm radius and adjusted its vertical position relative to the plasma.

Theoretically, for the confinement to restrict the plasma effectively, the plasma should be just in the center of the bowl. In this way, the spherical shockwave generated with it can be reflected by the confinement simultaneously to push the plasma into a more restricted volume. Therefore, higher energy is confined back into the core volume of the plasma, which better increases the plasma's parameters into a range with stable line intensity.

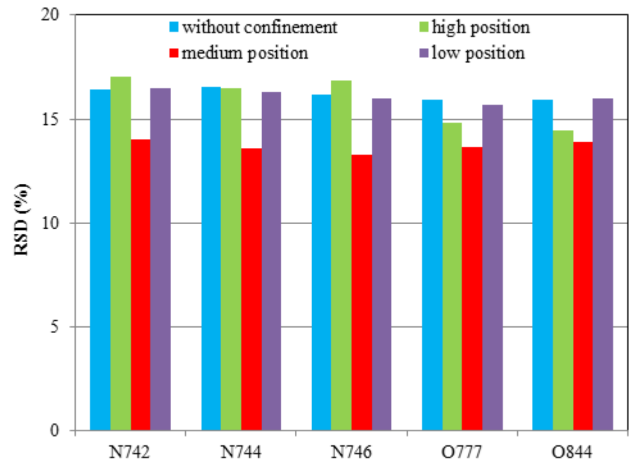

Fig. 5 RSDs with the bowl-shaped confinement at different vertical positions ('medium position' is where the confinement's center and the plasma's core coincide; 'high position' and 'low position' means the confinement is much higher or lower than its optimal position).

The comparison of pulse-to-pulse RSDs with the bowl-shaped confinement at different vertical positions, as shown in Fig. 5, verifies our above discussions. When the confinement is too much lower or higher than its optimal position, i.e., where the confinement's center and the plasma's core coincide, it can hardly reduce the signal fluctuations. Only in its optimized position, the bowl-shaped confinement can decrease the pulse-to-pulse RSDs by about 2~3%.

Besides its vertical position, confinement's size may also influence its plasma restriction effect. The results are shown in Fig. 6. With smaller confinement, the effect of stabilization of plasma core is more obvious. The pulse-to-pulse RSDs can be reduced from ~16% to ~12%.

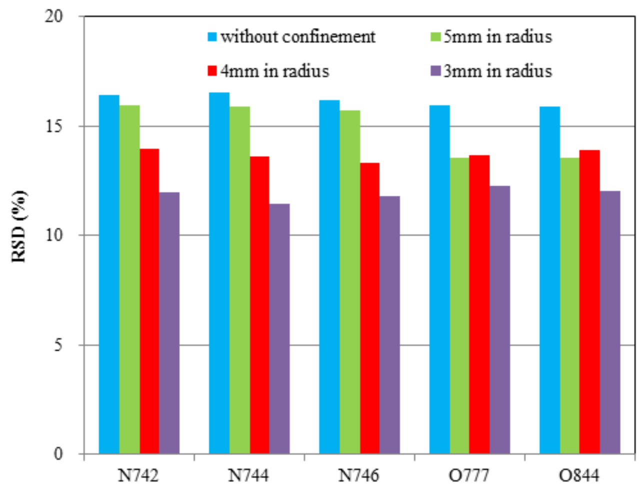

Fig. 6 Pulse-to-pulse RSDs with bowl-shaped confinement of different radius.

This result is reasonable that when the confinement is smaller, it can reflect more energy back to the plasma core with stronger confining effect. Taking the shockwave expansion velocity as typical as 10^5~10^6 cm/s, it takes 0.5~5 μs for the shockwave reflected back to the center. Thus a smaller bowl-shaped confinement will exert its influence during the earlier stage of plasma expansion, when the shockwaves are stronger.

However, too small bowl-shaped confinements will lead to direct contact between the confinement and the plasma and the effective area of the confinement will also become too small to reflect the accompanied shockwave.

Together with the previous part, we can see the physical shape and spatial location of the confinement play an important role on its stabilizing effect on LIBS signals in gaseous samples.

3.3 Verification of the stabilizing effect by ICCD images and SNR comparison

To further verify the bowl-shaped confinement's effect exerting on the plasma, we also compared the plasma images taken by ICCD camera with and without bowl-shaped confinement. For each case, 50 images were captured by ICCD camera with the same gate width and delay time as our spectrometers. Plasma morphology has been proven to be an effective method to study plasma dynamics during LIBS analysis.[29-30]

In Fig. 7 and Fig. 8, nine images of plasma (different laser pulses, same laser energy, delay time, and gate time) taken by ICCD with and without confinement are shown. We can see that the plasma's morphology in the cases with confinement are much more stable and regular in both the shape and the plasma position than those without confinement, verifying our previous expectation. Besides, we can also see a great variation in the plasma energy from these images.

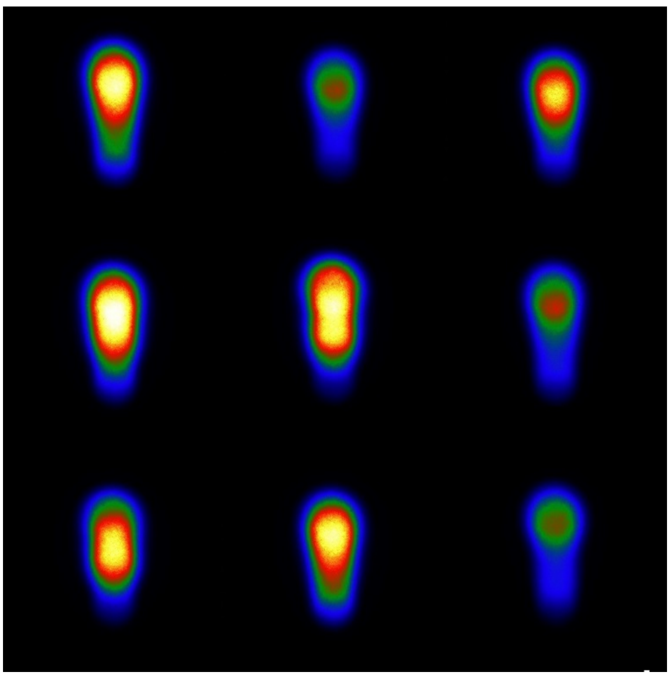

Fig. 7 Nine images taken by the ICCD camera without confinement at different pulses with same LIBS setup.

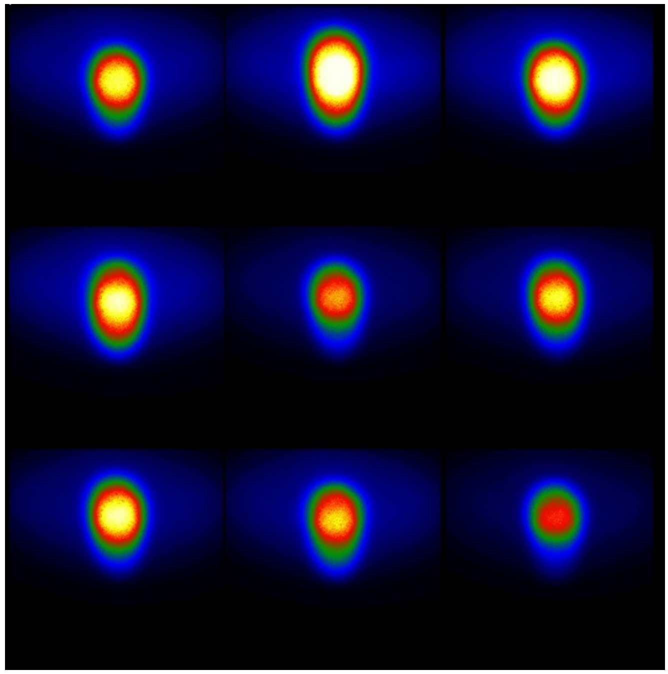

Fig. 8 Nine images taken by the ICCD camera with bowl-shaped confinement at different pulses with same LIBS setup.

To confirm the stabilizing effect of the bowl-shaped confinement more clearly, we calculate and sketch the pulse-to-pulse averaged counts and RSDs of the plasma images taken by ICCD (50 images for each case) with and without confinement as shown in Fig. 9 and Fig. 10, in which the RSDs of counts are calculated pixel by pixel to find out the fluctuations of plasma position and brightness.

From the comparison of the averaged counts image with and without confinement, we can see the bowl-shaped confinement restricted the plasma to a more regular spherical shape around its core. A regular plasma is good for us to collect signals from plasma by fibers or lens when the plasma energy becomes more focused. We can also see the plasma core becomes brighter with the bowl-shaped confinement, which confirms our comparison of line interties.

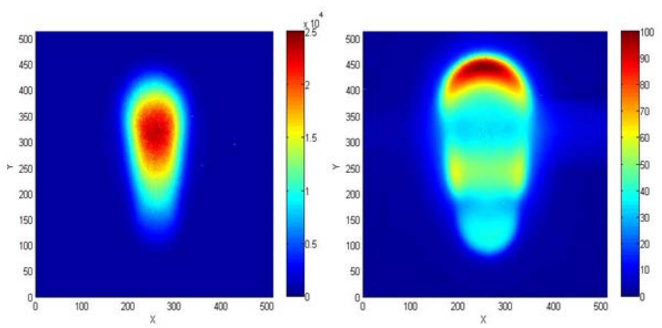

Fig. 9 Plasma images taken by ICCD without confinement, (a) Averaged counts image (b) Pulse-to-pulse RSD image.

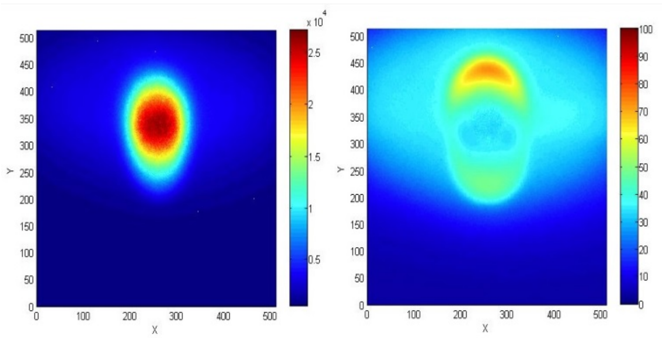

Fig. 10 Plasma images taken by ICCD with bowl-shaped confinement, (a) Averaged counts image (b) Pulse-to-pulse RSD image.

From the comparison of pulse-to-pulse RSD images with and without confinement, it is clear that the overall fluctuation of plasma has been reduced by about 20%, especially the upper part of the plasma image. Fluctuations in this part mainly come from plasma positions' variations along the vertical axis; thus when the confinement is in its optimal position where its center coincides with plasma's core, plasma's position becomes more stabilized. Furthermore, the stable area of the plasma core becomes larger with the bowl-shaped confinement, which is beneficial for the signal collection.

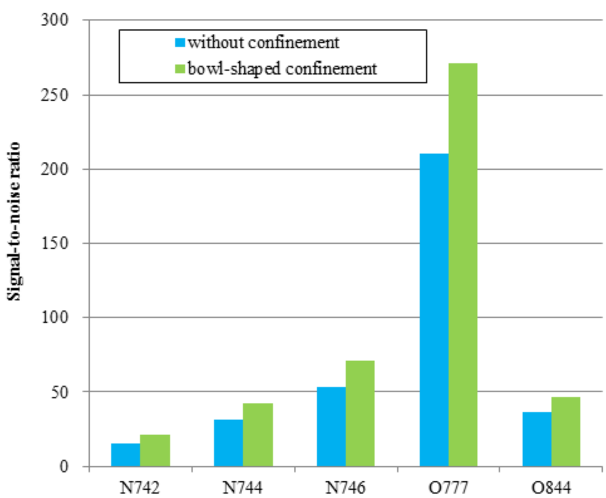

Fig. 11 SNRs with and without confinement.

We also calculate the signal-to-noise ratio (SNR) for the selected spectral lines with or without confinement. Results are shown in Fig. 11. From the comparison, the bowl-shaped confinement improves the SNRs by about ~30% for both nitrogen and oxygen. This improvement means a lower limit of detection could be achieved by using bowl-shaped confinements.

3.4 Normalized and group RSDs with bowl-shaped confinement

Bowl-shaped confinements stabilize the signals by confining plasma energy in a more restricted area and stabilizing the plasma's position. However, as analysed before, another source of instability is the different proportion of laser energy absorbed by plasma generated in gases. This kind of energy fluctuations can be seen in Fig. 10(b), where the RSD of background in the confinement is between 30% and 40%, contributed by differences in plasma energy. Dealing with this influence, signals are normalized with whole spectral area. Normalized RSDs can reach 2.97% for N742 and 3.94% for O777, from 11.96% and 12.25% without normalization respectively, as shown in Fig. 12.

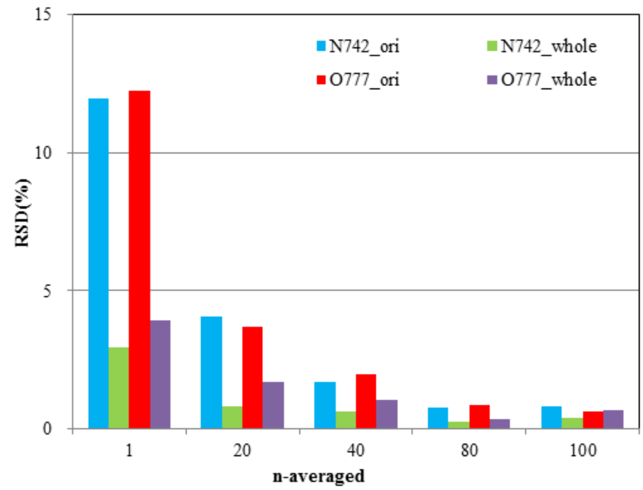

Fig. 12 Inter-group RSDs with bowl-shaped confinement and spectra normalization.

We also study the inter-group RSDs by averaging the spectra in groups of different sizes. From Fig. 12, we can see that the group RSDs can reach lower level when more spectra are averaged. By averaging 80 measurements, the group RSDs for N742 and O777 normalized intensity can be reduced to 0.28% and 0.35%.

The spectra accumulating or averaging method has been used by most researchers[10-12] before. In this way, higher signal-to-noise ratio (SNR) and lower limit of detection (LOD) are obtained. However, the capability of these methods is limited by 'real' fluctuations occurring in the experiments. In fact, the inter-group RSD will not be decreased any more when the number of spectra to be accumulated or averaged exceeds some extent.

As shown in Fig. 12, when the size of group exceeds 80, the RSD cannot be reduced any more. In previous literatures, inter-group RSDs cannot be reduced to such level because 'real fluctuations' of plasma signals in experiments limit the potential of spectra averaging or accumulating method. It should also be noted that by utilizing our method, analytical performance of LIBS analysis of pure gas is comparable with its analysis of solids or liquids.

In addition, we have compared the current results with previous studies. The comparison was shown in the following table. As shown, the utilization of bowl-shaped confinement improved the measurement repeatability for gas analysis using LIBS.

Table 1 Representative RSDs of gas-phase analysis using LIBS

Elements	Environment	RSD (%)	LOD (p.p.m.)	Ref.	Comments on RSD reduction method
Cl, F	air	8	Cl, 8; F, 38	12	16-averaged RSD
Cl in CCl_4	air	unreported	1.5	3	
F, Cl, S, O	air	F, 7; Cl, 12; C, 8; S, 7;	F, 20; Cl, 90; C, 36; S, 1500;	11	1000-accumulated RSD
F	air/He	unreported	40 (in air); 0.3 (in He);	2	
H_2	N_2	unreported	20	5	
Ar, He	N_2	unreported	Ar, 17; He, 57;	6	
O, H	air	unreported	O, 15; H, 10;	4	
N_2, Ar, O_2, He	H_2	unreported	N_2, 80; Ar, 97; O_2, 10; He, 25;	7	
CO_2	air	3.6	36	10	5-averaged RSD with 40 on-chip accumulation for each measurement, using metal substrate to provide initial electrons.
Ar, Kr, Xe	pure gas	Ar, 2.5; Kr, 1.2; Xe, 2;	unreported	28	Using fs-laser to achieve high stability breakdown.
H, C, N	HEPA filtered air	H, 26; C, 15.8; N, 2.52	unreported	14	Using P/B to calculate single-pulse RSD in HEPA filtered air for seeded laser operation.

Conclusions

In this work, we tried to improve signal stability during LIBS analysis of gaseous samples. From related literatures, we concluded that there are three main sources of fluctuations: (1) varied plasma positions due to existing of floating particles, (2) different proportion of laser energy absorbed by plasmas, and (3) variations of plasma shape and size. Based on this understanding, with aid of ICCD images, we designed a bowl-shaped confinement to increase signal stability by stabilizing the core of plasma and confining plasma energy in a more restricted area. With normalization with whole spectral area to alleviate the absorbed energy difference, our pulse-to-pulse RSDs for nitrogen and oxygen can reach 2.97% and 3.94%, 80-averaged group RSDs for nitrogen and oxygen can reach 0.28% and 0.35%. The result is comparable with solid analysis by LIBS, making quantitative analysis of gaseous samples more reliable.

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Notes and references

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