Absolute Analysis of Particulate Materials by Laser-Induced Breakdown Spectroscopy

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We have developed a new data acquisition approach followed by a suitable data analysis for Laser-induced breakdown spectroscopy. It provides *absolute* concentrations of elements in particulate materials (e.g., industrial dusts and soils). In contrast to the known calibration procedures (based on the ratio of spectral lines), which are applicable only when one component is constant, this approach requires no constant constituent and results in absolute (rather than relative) concentrations. Thus, the major drawback of this analytical method, namely, the signals' instability (especially when particulate materials are concerned) is partially solved. Unlike the commonly used integrated data acquisition, we use a sequence of signals from *single* breakdown events. We compensate for pulse to pulse fluctuations in an intrinsic way, and the final results do not depend on the presence of any constant component. Extended linear calibration curves are obtained, and limits of detection are improved by 1 order of magnitude relative to previous methods applied to the same samples (e.g., detection limit of 10^{-12} g of Zn in aerosol samples). The proposed compensation for pulse variations is based on the assumption that they can be described as a multiplicative effect for both the spectral peaks and a component of the baseline. In other words, we assume that the same fluctuation pattern observed in the spectral peaks is present in the baseline as well. This assumption is shown to hold and is utilized in the proposed method. In addition, a proper data-filtering process, which eliminates ill-conditioned spectra, is shown to partially compensate for problems due to the nature of analysis of particulate materials.

Laser-induced breakdown spectroscopy (LIBS) is a well-established analytical method.[1-5] It is based on plasma formation on the surface of analyzed samples, by means of focused laser pulses. The plasma samples the substrate and excites its atoms. The light emitted from the plasma at a certain time delay after the laser shot is spectrally analyzed. Detailed investigations of the various processes involved in this method have already been carried out.[6-28] The method has been applied to many matrixes and samples, although the best results were obtained from solid and hard surface materials, such as metals and alloys.[29-32] Several new developments of the LIBS method have been extensively studied and reported.[11-12,33,34]

The main advantage of the LIBS technique is that, without laborious chemical preparations, it provides direct chemical analysis of solids. Only optical access to the sample is required, and sample contamination-induced risks are minimal. The method is very promising for potential industrial applications, where on-line analysis is requested, and it can be applied to a variety of environmental analyses as well. Actually, a method to analyze heavy metals in sand and soil has been recently developed and reported.[6] The current limits of detection depend on the matrix in hand and on the analyzed elements. Generally speaking, detection limits vary from the ppm range (metals) to the 50 ppm

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range (soils) and up to the percentage range (gases and airborne aerosols).

In spite of its simplicity, not many industrial applications are currently available. The reason is that the major drawback of LIBS is related to the stability of the spectroscopic plasma signals: These undergo considerable fluctuations that originate from the very nature of the method. The laser intensity fluctuates within 1−5% and the scattered light depends on the local matrix effects and on physical and chemical characteristics. The geometrical parameters also vary during the measurement, due to the surface crater formation.[5,6,8−10] Solid humidity variations as well as the atmospheric composition and even the sample's color also contribute to the observed signal fluctuations. Hence, the laser ablation, a highly nonlinear process, is dramatically influenced by the above. In the case of aerosol analysis, these fluctuations are even higher, since plasma location is not stabilized properly (it may occur at different positions along the laser beam).

The most common method to partially compensate for signal fluctuations in LIBS method is based on calculating the ratio of the spectral peak intensity to that of the reference intensity. Assuming a constant concentration of such reference element in all samples of interest, this ratio partially accounts for some of the variations, provided that the same multiplicative fluctuation is valid for both the analyzed and the reference peaks. Most analytical achievements have been recently obtained by utilizing such an internal calibration method.

The obvious drawback of the currently used internal calibration is that relative, rather than absolute, concentrations are obtained. Moreover, in many applications there is no such reference component in the system; thus, this type of internal calibration cannot be carried out at all. Thus, a different approach to this issue is of considerable importance and significance.

A somewhat general approach to signal fluctuations, namely, integration over many laser shots, helps only partially. Detailed noise analysis of LIBS methods proved that signal integration improves results much less than $N^{1/2}$.[6] The improvement due to signal integration is "saturated" after ~50 shots and is not very significant anyhow. The reasons for this behavior originate from the nonlinear ablation effects (that actually magnify fluctuations) and from some instrumental noise components.[6]

In this paper, we describe a new data acquisition and analysis method that eventually compensates for a major part of intrinsic fluctuations found in LIBS signals. It is based on analysis of single-shot measurements rather than on integrated ones. Data from each single shot are properly treated, prior to their application. It is assumed that the variations can be described as a multiplicative effect for both the spectral peaks and a baseline component. In this way, fluctuations are accounted for, with no explicit dependence on a reference component. The proposed method eventually improves results by 1 order of magnitude. It also provides such calibration routines that allow absolute concentrations to be obtained.

EXPERIMENTAL SECTION

Experimental Setup. The experimental arrangement is shown in Figure 1. The plasma excitation was carried out with a Q-switched Nd:YAG laser (Continuum) operated at its fundamental wavelength (1060 nm), at a repetition rate of 0.2 Hz (to prevent signal change due to aerosol production). Pulse energy was ~300 mJ and pulse duration was 7 ns. For soil analysis, the light was focused with a plano-convex quartz lens of $f = 400$ mm. The solid
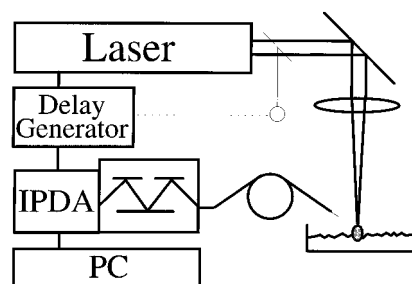

Figure 1. Experimental setup for time-resolved LIBS.

samples were positioned ~50 mm above the focal point, in order to minimize sensitivity to the exact geometrical position. For aerosol analysis, a lens of $f = 200$ mm was used, in order to avoid creation of plasmas away of the focal point. Under these experimental conditions, small particulates (<1 μm) are believed to be completely vaporized, while larger ones are only partially sampled.[6] The light from the plasma was collected by an optical fiber (quartz and silica PCS 600 B multimode, step index), which was placed ~10 mm apart the primary interaction regime. This geometry provides a wide collection angle that covers most of the plasma emission and also prevents damaging the input surface of the fiber by dust and ablated materials. The light from the fiber was introduced into the entrance slit of a spectrometer (ARC, SP 250). The spectra were recorded and temporally resolved by an intensified photodiode array analyzer (Princeton Instruments), consisting of 1024 elements intensified by a 25 mm multichannel intensifier. The temporal response of this detector is of ~6 ns. Data acquisition was performed at 12 bits.

Sample Preparation. Several samples were analyzed with this experimental arrangement. These include locally collected soils (slightly pressed prior to direct analysis) and dense aerosols, produced by mechanical agitation of dry powderlike material (particle size distribution of ~10 μm, $\sigma \cong 6 \mu$m). The soil samples were placed in a flat dish that was rotated in order to provide a fresh site for each laser pulse. Aerosols were measured directly in a glass vessel, where they were mechanically stirred and created. Measurements were carried out upon establishment of steady state conditions.

Sample Contamination and Analysis. The contamination of the locally collected samples with heavy metals was carried out by mixtures of standard solutions: Solutions of known heavy metal concentrations were added to the solid samples, stirred, and then dried at 95 °C (to avoid water boiling). The middy mixture of solid sample and spiking solution was prepared such that it can be easily stirred to ensure uniform contamination of the solid particulates. At the end, the samples were ground with a mortar. These spiked standards were prepared for external calibration, for analysis of unknown samples. Each standard was analyzed by digestion in aqua regia, according to DIN 38414[35] and analyzed by AAS as a reference method for Zn.

The so-prepared standards were uniformly spiked (particulate to particulate), however, not necessarily within a single particulate. This contamination feature is well-known (as well as its size distribution dependence), and its effect upon the LIBS signal from particulate samples has been studied and understood.[6,8−11] Thus, these effects are out of the scope of the current research.

(35) Aufschluss mit Königwasser zur nachfolgenden Bestimmung des säurelöslichen Anteils von Metallen (S7), DIN 38414, part 7. In *Vom Wasser*; Beuth Verlag: Berlin, 1982; Vol. 58, pp 395−397.
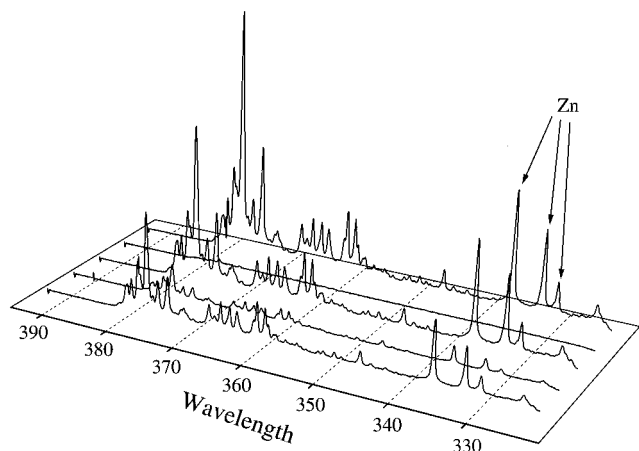
Figure 2. Four spectra of Zn-contaminated aerosol, obtained in a sequence of single-shot measurements. Note the pulse fluctuations. The three Zn lines used in this study are indicated.
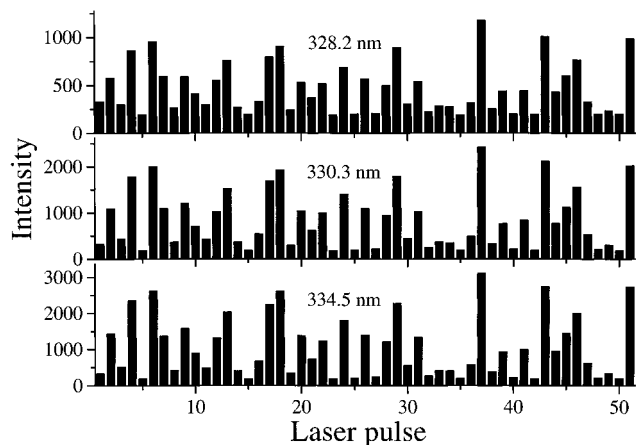

Figure 3. Spectral intensities of three Zn lines, obtained from a sequence of 50 lasers shots. In spite of the extensive pulse fluctuations, all three peaks undergo the same variations.

Software. Software for data analysis and evaluation programs were written in FORTRAN 77 and compiled by an MS-FORTRAN Power Station 1.0. Data acquisition and analysis were carried out on a PC (80486 CPU).

RESULTS AND DISCUSSION

Inspection of Single-Shot Spectra. The initial idea behind this study was to observe spectra originating from single laser pulses in order to identify a possible fluctuation compensation routine. Figure 2 shows four spectra of Zn-contaminated aerosol, all measured under the same experimental conditions. Three Zn peaks are present in this range, as shown (Actually, the peak at 330.3 nm is composed of two unresolved lines at 330.259 and 330.294 nm. The peak at 334.5 nm is composed of three unresolved lines at 334.502, 334.557, and 334.493 nm.) The extensive pulse-to-pulse fluctuations are clearly observed. (Their origin has been already studied and discussed.[6,11]) Actually, one spectrum is so weak that it would mainly contribute noise to a signal-averaging process (It probably originates from a plasma event that took place away from the focus and out of the measurement volume).

Figure 3 shows the spectral intensities of these three Zn lines, obtained from a sequence of 50 lasers shots. The average signals (integrated over these 50 pulses) obey the expected ratio of these
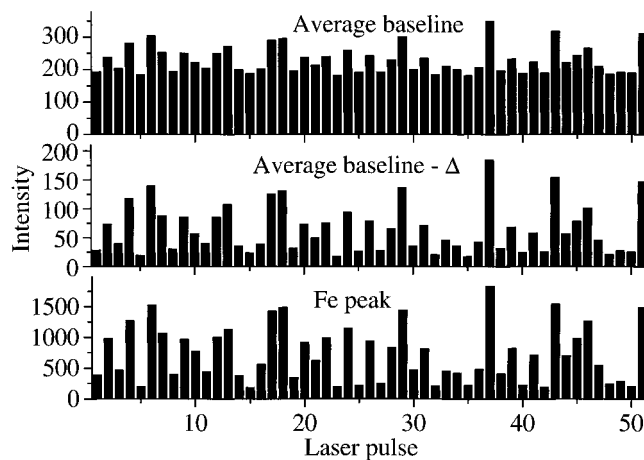

Figure 4. Sequence of the average baseline, for 50 shots (upper panel), and the result of subtracting a constant value (middle panel). These spectral intensities are compared to those of a Fe peak for the same pulse sequence (lower panel). A component of the baseline undergoes the same fluctuations as the spectral peaks.

spectral lines. However, a visual comparison of the fluctuations points out a major similarity between these signals: When one line is exceptionally intense, so are the others. In fact, almost all spectral lines show a very similar behavior.

We have also observed that the average baseline exhibits a very closely related fluctuational pattern. The average baseline was measured as the average signal over all detector pixels where no spectral peak was present (e.g., most pixels in the range 323–327, 337–339, 344–346, 349–350, and 365–366 nm). The sequence of the average baseline, for the same 50 shots, is shown in the upper panel of Figure 4. We illustrate that by subtracting a constant value of the average baseline, one can actually reproduce the signal variation pattern of almost any spectral line. The average baseline minus a constant value is shown in Figure 4 (middle) and compared to a peak of Fe (for the same pulse sequence). Obviously, a part of the baseline undergoes the same fluctuations as the LIBS spectral peaks, and this information is utilized in the forthcoming data analysis. (In this particular case, the constant subtracted value was calculated by two-parametric least-squares fitting to a Fe peak at 374.9 nm. One of the parameters was the constant value, and the other was a multiplication factor. The actual parameters are not of importance, since this calculation is performed for presentation purposes and is not a part of the proposed algorithm.)

Additional important information is provided by a histogram of the intensities at a Zn line (from a relatively high concentration sample), as presented in Figure 5. A reasonable distribution around a certain intensity is observed; however, the probability of obtaining a very weak peak (close to zero intensity) is much higher than expected. These events occur due to geometrical reasons or experimental artifacts, and it is clear from this figure that they should be eliminated from any data analysis program. As will be shown in the following, such data filtering procedure is also justified in terms of the observed baseline behavior.

Theory. In order to take advantage of the above findings, we need to find a correct model that provides an explanation. Then, we can use this model to compensate for the observed fluctuations.

As seen in Figure 4, we assume that the actual baseline B_i, measured at shot i, is given as a sum of a constant (though sample-dependent) baseline b_0 and an individual contribution, b_i, that
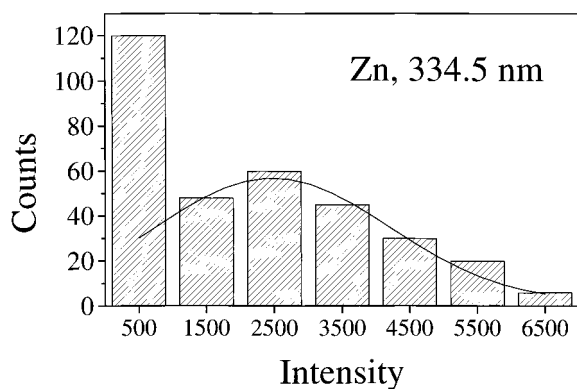
Figure 5. Histogram of the spectral intensities at 334.5 nm (Zn lines). The probability of obtaining a very weak peak is much higher than predicted by the distribution at other intensities.

characterizes the shot i:

$$B_i = b_0 + b_i \qquad (1)$$

The individual concentration-independent contribution, b_i, originates from the fact that each pulse is different (e.g., in its available energy). This contribution indicates the fluctuational status of the shot of interest. Let us assume that fluctuations are of multiplicative nature, which means that b_i can be presented as following:

$$b_i = k_1 f_i \qquad (2)$$

where f_i is a factor that is responsible for the signal and baseline fluctuations and k_1 is a proportionality factor.

When looking on a spectral peak of an element, P_i (of pulse i), one can describe the signal as a sum of the baseline of the same pulse i and the spectral intensity that is proportional to the concentration of the element, C. Again, we must assume that the same multiplicative factor f, found at the baseline, that represents the fluctuation effect is applied to the spectral peak as well:

$$P_i = B_i + Ck_2 f_i \qquad (3)$$

Substituting b_i of eq 2 in eq 1, and then substituting the resulted expression of f_i into eq 3, provides

$$P_i = B_i(1 + kC) - kCb_0 \qquad (4)$$

where $k = k_2/k_1$.

Thus, a plot of the peak intensity P_i against the average baseline intensity B_i should provide a straight line with a slope $\alpha = 1 + kC$. Therefore, a plot of $\alpha - 1$ against the concentration C would result in a linear calibration curve passing through the origin and free of fluctuational effects. This calibration plot can replace the traditional calibration of the signal against concentration. It takes into account the shot-to-shot fluctuations in an intrinsic manner; therefore, this calibration curve is expected to be more linear and to provide better results.

The calibration routine previously described is suitable to a data acquisition method involving a sequence of single-pulse measurements. Thus, a similar set of measurements is also required for the unknown sample. Although this method is expected to provide the best results, in some cases analytical results must be based on a single laser pulse (e.g., when fast on-line results are required). For this cae, a modified calibration and prediction procedure is suggested.

Assuming that b_0 is given by the average baseline, $\hat{B}_i$, we obtain from eq 3 the following calibrating equation:

$$S_i = \frac{P_i - B_i}{B_i - \hat{B}_i} = Ck \qquad (5)$$

S_i is a quantity that is proportional to the concentration (defined by eq 5); thus, this linear plot can be used for concentration prediction using a *single* pulse. This method cannot provide the same quality of prediction as the previous one, since it is based on a single pulse only. Nevertheless, this calibration scheme is based on the correct baseline behavior and should provide better results than traditional methods. It should be noted that the assumption that b_0 is the average baseline is commonly correct, but not necessary. The previous calibration routine, which is based on a sequence of laser shots, does not require any assumption regarding the distribution of the baselines.

The above assumptions used in eq 4, which are justified by experimental observations, can be understood in terms of well-known formulas in plasma physics. The absolute intensity of the plasma continuum in a given small wavelength interval, for free-free and free-bounded electron transitions, in the field of ions of element a, is proportional to $N_e N_a^z$ where N_e is the electron density, N_a is the ion density, and z is the ion's charge (equal to 1 in our application).[36] Thus, f_i (in eq 3) may be regarded as a function of N_e, which is itself a strongly nonlinear function of the laser output power density. The variations of f_i are thus attributed to variations of N_e. The parameter b_0 (in eq 1) is regarded as the laser output-independent part of the plasma continuum emission, which may originate from air plasma emission and from instrumental noise.

The reason that the same factor f_i holds for both eqs 1 and 3 is that the analyte line intensities have the same functional dependence on N_e as the continuum emission. This fact can be easily seen from the formula describing the ratio of the full intensity of any analyte spectral line to the absolute intensity of the plasma continuum (provided in ref 36). This ratio is a function of the oscillator strength, the energy of the lower state, statistical weight, and ionization energies; however, it is *not* a function of N_e. It is also a function of the temperature, which is only slightly varied, in our case.

The electron density, N_e, is directly related to the ionization potential of the matrix components. Thus, when variation in the concentration of an element with high ionization potential is concerned, it is important to check that the matrix in hand consists of easily ionized elements. Actually, this is the case in our study, where Zn concentration is analyzed in a very wide concentration range (up to 40%). The linearity of the calibration plots is related to the presence of Al, Ca, and Fe, which are easily ionized and are responsible to the electron density.

Application to Aerosol Analysis. In order to test the applicability of eq 4, we plotted the peak intensity of Zn line as a function of the average baseline, for a sequence of 50 laser pulses.

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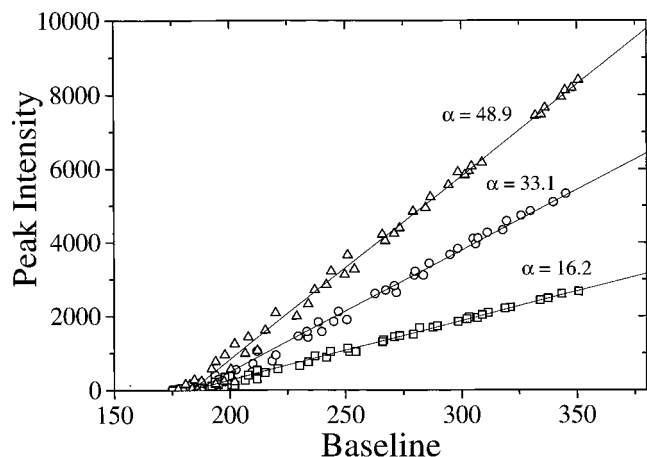
Figure 6. Peak intensity of a Zn spectral line as a function of the average baseline, for a sequence of 50 laser pulses. Each curve corresponds to a different Zn concentration. The slopes, α, are recorded for the calibration plots.
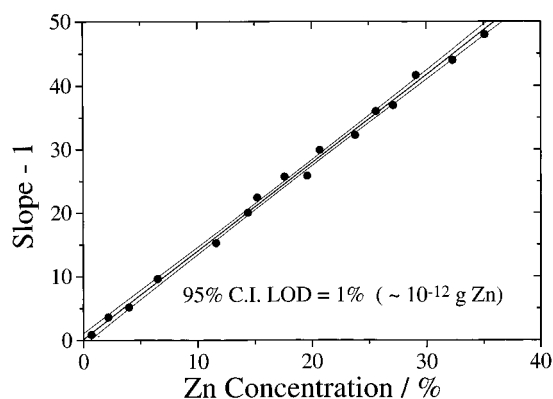

Figure 7. Plot of α − 1 against Zn concentration in aerosol. The 95% confidence intervals and the calculated LOD (based on these intervals) are indicated.

The results are shown in Figure 6, for three different Zn concentrations. The linearity of the curves is self-evident as is anticipated by eq 4.

The calculation of the slope α, however, should take into account the general findings of Figure 5. In view of these results, we decided to omit all weak peaks from the calculation of the slope and to give a slightly increasing weight to the points as they represent more intense peaks. Actually, omission of these weak peaks is equivalent to omission of all peaks whose baseline is lower than the average baseline. This data filtering out is obvious from eq 5, where negative values are rejected.

Now, according to the proposed model, a plot of α-1 against concentration should provide a linear calibration, through the origin. This calibration plot is shown in Figure 7, together with the 95% confidence intervals and the calculated limit of detection (LOD). These results have to be compared to the traditional calibration plot that is obtained from the integrated signal (over the same 50 shots). This calibration plot is shown in Figure 8. The 95% confidence interval based LOD is 10 times higher thna that of Figure 7. The spread of the data is considerably higher, since in this case we do not compensate correctly for pulse to pulse variations (except of a partial averaging effect).

Application to Soil Analysis. Heavy metals in soils have to be analyzed in the ppm concentration range. The calibration plot (slope − 1 vs concentration) for Cd in soil, as obtained by the
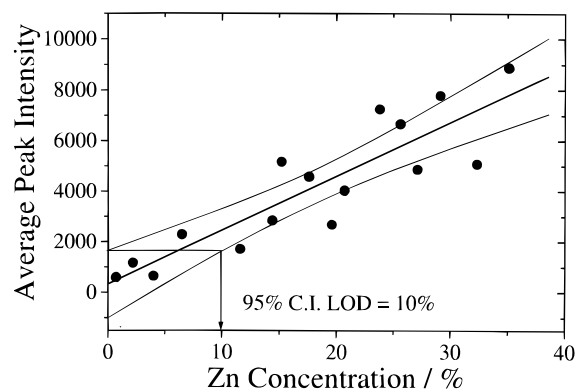

Figure 8. Calibration plot for Zn in aerosols obtained from the integrated signals (over 50 shots). The 95% confidence intervals and the corresponding LOD are shown. The spread of the data is considerbly higher than in Figure 7.

proposed method, is linear up to 600 ppm. The resulted 95% confidence interval based LOD is 18 ppm. These results should be compared to the traditional calibration plot obtained from the same 50 shots, using signal averaging: The points in this curve are much more scattered. The resulted 95% confidence interval based LOD is 150 ppm in this case. Again, the proposed calibration method provides a considerable improvement.

It should be noted, however, that the above calibration plot does not pass through the origin, as expected by the proposed model. Actually, even more severe deviations were found in other cases of soil analysis. As long as the slopes are high (as in the aerosol analysis measurement series), deviations from origin are hardly observed. When slopes are low (as found in some soil analysis measurements) the discrepancy becomes clear. It means that the simple proposed model cannot explain all experimental features. Further investigation is required for understanding these effects. Nevertheless, the calibration plot is reasonably linear and can be applied for analytical purposes.

Comparison to Analog Integration. For methodological reasons, we preferred to compare the new method to the traditional method using the same data set. However, in some experimental setups, the traditional method that is based on signal averaging may provide better results: This happens when the signals are weak and "on-target" integration is possible. It means that the integration is carried out in an analog way on the detector itself, and in this case, the readout noise is reduced. If the detector is cooled, the readout noise becomes the most significant component, and in such a case, the traditional results may become better. Moreover, even then, one can usually increase the signal (e.g., by increasing the laser energy or by modifying the optical geometry) and move to the range where better results are obtained with the proposed method. In all cases, if the signals from single shots are high (relative to the saturation limit of the detector), the proposed method must provide better results (since no analog integration is possible). In most experimental setups, such conditions can be achieved easily.

CONCLUSIONS

A method for compensating for shot-to-shot variations in LIBS analysis has been established and evaluated. This method has been based on the observation that a part of the average background undergoes the same pattern of variations as the spectral signals. A model has been developed, where the

variations are assumed to be of multiplicative nature. This model leads to the conclusion that a plot of the slope of the peak intensity minus baseline (for a sequence of shots) against concentration should be linear and thereof utilized for calibration purposes. The model was found to be valid for LIBS spectra.

The calibration plots obtained in this method are shown to be better than the traditional plots. Actually, LOD values in this method are improved by 1 order of magnitude. Moreover, the proposed method provides *absolute* concentrations, while traditional LIBS has provided relative values (due to poor performance for absolute values). The method does not require an internal standard element of known concentration; however, standard samples are still needed to obtain calibration curves.

Apparently, the proposed data acquisition method involves many single-pulse measurements, which may take a longer time than normal averaging. Indeed, signal averaging at a higher laser repetition rate (say, 50 Hz) is faster, since at such rates the bottleneck is the CCD readout time. Nevertheless, in most applications signal averaging at high repetition rates is not appropriate anyhow: plasma production at high rates causes changes to the measurement environment (e.g., aerosol generation), which affects the results (e.g., by screening the incoming laser beam). Moreover, due to local crater formation, one prefers a moderate repetition rate that allows for refreshing the sample. Thus, the lower repetition rate imposed by the readout time in single-shot measurements does not affect the overall measurement duration.

As previously mentioned, in this study we can only prove an improved precision and we cannot deduce about any accuracy improvement. The accuracy of the LIBS method (which could be investigated by analyzing a standard reference material using our calibration curves) is a complicated issue which has to be with matrix effects. These are not well understood yet and were not studied here. (A study of matrix effects in LIBS and their influence on analytical accuracy is planned.)

This method is especially valuable for particulate analysis, where signal fluctuations are severe. The most difficult case in this sense is aerosol analysis, where additional effects are introduced by the instability of the plasma location.