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Direct Aerosol Analysis by Time Resolved Laser Plasma Spectroscopy - Improvement by Single Shot Measurements

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Abstract : Environmental and industrial aerosols can be analyzed on-line by laser plasma spectroscopy. The main problem in direct (no preparation or presorting) aerosol analysis is the extensive spectral fluctuations. A method to partially solve this problem is proposed. It is based on single shot measurements and application of a special rejection algorithm. The major factors that influence the spectral variations are discussed, in relation to the correction possibility by a rejection program. The method works well when average intensity of the single spectra is relatively high, as compared to detector's saturation limit. If intensities are too low, the accumulation of readout noise is critical, and no improvement is expected.

Keywords : Aerosols, Laser Plasma Spectroscopy, Analysis, Detector.

1. Introduction

Aerosol analysis is one of the most relevant means of environmental protection, yet, it is also one of the most difficult tasks. While some on-line methods for air and water analysis are already available, no such method has been largely introduced for aerosols (and for solid environmental samples). Concerning the possible hazards, contaminated aerosols are usually considered more dangerous as compared to gaseous contaminations. Single aerosol particles may contain very high concentrations of hazardous materials (such as heavy metals, or PAH - Polycyclic Aromatic Hydrocarbons). They may be transported for long distances, and then be deposited in human lungs by breathing. Traditional analytical methods require collection of aerosols on filters, and chemical analysis that is carried out after a proper chemical treatment.

These methods provide information *after* the damage has already been caused, thus, on line methods are needed. Such new methods could be applied, for example, in the mouse of a chimney, to provide a fast feedback. In addition to the environmental interest there is a considerable industrial attention to on-line aerosol analysis. Many industries, such as steel factories, could take advantage of on line aerosol analysis. One of the methods that has the potential to provide on-line aerosol analysis (as well as other environmental samples), is the Time Resolved Laser Plasma Spectroscopy (TR-LPS).

TR-LPS is a well established analytical method, that has been mostly applied to solid surfaces, such as metals and ceramics[1-10]. In this method a laser pulse is focused onto the analyte to produce a hot spark (plasma spot). The plasma, which reaches a temperature of ca. 20,000°K, ablates some material and excites its atoms. The analysis is based on the spectrum emitted from the plasma plume. Temporal resolution is required, since the spectral lines can be resolved, and are of analytical value, only after a certain delay and for a certain duration. This method has been profoundly investigated, with respect to many effects and factors that influence the results[11-39]. These include the effect of the laser energy, timing of the spectral measurement, humidity and matrix effects, and the gas above the sample. Several applications to analysis of solid environmental samples, such as sand, soils, and sediments, have been developed[10]. The method has also been tested for pollutant concentrations in air (chlorine and fluorine)[40]. An attempt to analyze particulates in combustion environments has been carried out[28].

Generally, the performance of the TR-LPS method is the best when flat solid and homogeneous samples are analyzed. In this case detection limits in the sub ppm range are easily obtained[4]. Application to soils, sands and sediments provided detection limits in the range of 10 ppm[10]. Analysis of halogens in clean air, under optimal laboratory conditions, provided detection limits of 10-30 ppm[40]. Only qualitative and semi-quantitative results could be obtained in analysis of particulates in combustion environments[28].

This paper is focused on direct analysis of aerosols from industrial origin. Since the method is designed for on-line and in-situ analysis, no sample preparation and no sorting (by particulates' size or composition) have been carried out. Results have been improved by application of single pulse statistics and chemometric methods. Absolute concentrations are provided from linear calibration plots, without application of any internal calibration method.

2. Experimental

The experimental design includes a Nd:YAG laser (150 mJ / 7 ns) and an intensified photodiode array spectrometer (OMA system). Similar experimental setups have been previously described in details[e.g.10].

Aerosols were produced from solid deposition collected from a steel factory line. This oxidized material included high concentrations of Fe, Ca, Zn and Pb. (On line composition information is of great industrial interest.) Variations of concentrations were in the percentage range, which defines the relevant analytical performance in such applications. In order to simulate industrial aerosols, the solid dusty materials were introduced in opened chambers and fine aerosols were produced by mechanical mixing. No drying was carried out. Measurements were performed under steady state conditions.

Data were collected from single shots, and transferred to computer files. In some cases, accumulation on the photodiode array, of ca. 100 pulses, has been carried out, for comparison with single shot analysis. Delay and integration times were optimized for best signal to noise ratio.

Reference analyses were carried out by Atomic Absorption Spectroscopy of the solid materials.

A special data analysis program has been developed. This program compensates for the intense background emission, reconstructs the spectral peaks, and performs a special rejection algorithm. All codes were written in FORTRAN, and compiled with MS Power-Station 32 bit compiler. Data analysis program

was run on a PC (Pentium processor), under Windows environment.

3. Results and Discussion

TR-LPS spectra are known to be relatively problematic, concerning data analysis. For example, all TR-LPS spectra have considerable nonlinear baselines[10]. Also the shape of the peaks are complex, and cannot be easily reconstructed. This is a results of the measurement system (intensified photodiode array), and the extreme plasma conditions (temperature, pressure change, etc.). TR-LPS spectra of aerosols are even more problematic. Several representative spectra are shown in Figure 1a. The intense plasma background is always present, even without the presence of aerosol particles. Thus, these two factors must be handled prior to any data analysis. Figure 1b shows typical TR-LPS spectra of soil sample, in order to point out the differences in baselines, and to emphasize the special problem in aerosol analysis.

The background has been subtracted in two ways: In the first method, a function has been fitted to the *shape* of the background, that is, to the spectra obtained from air plasma. The problem is that due to reasons described in the following, TR-LPS spectra undergo extensive fluctuations. Some spectra are week, and some are intense. Thus, a single background cannot be fitted to all spectra. Therefore, a function that has the shape of the background has been numerically fitted to each spectrum. It has been "blown" or "shrunk" to fit the actual baseline of each individual spectrum. This procedure has been carried out such that the least squares of the difference between the baseline function and the actual baseline (defined in a certain spectral range where no analytical lines are present), is minimized. Then, the new baseline is subtracted from the spectrum.

In the second method, the baseline function has been kept constant, and the spectra have been fitted to this baseline, in the range where no peaks are present. Again, this fitting was carried out to minimize the least squares. No advantage of the second method over the first one has been observed, thus the first method has been adopted.

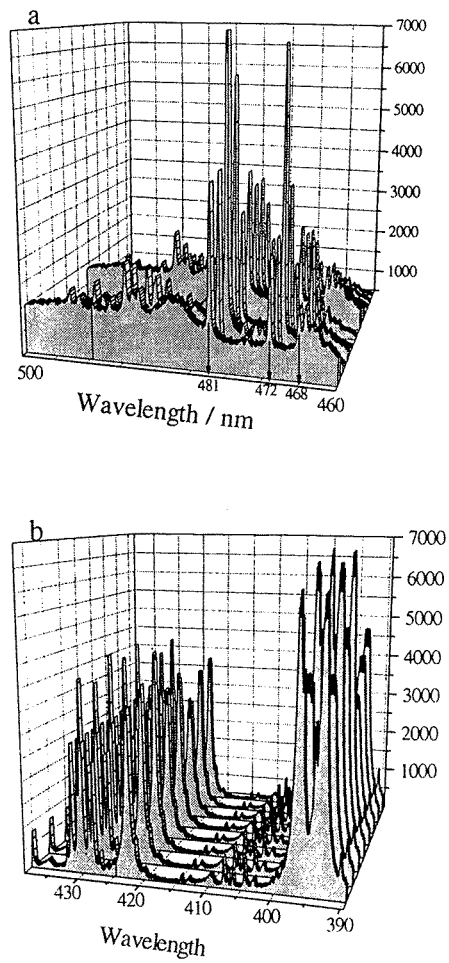

Fig. 1. Representative LPS spectra (a)aerosol (b) soil

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After baseline correction, the relevant peaks have been reconstructed to provide corrected intensities.

Reconstruction is required since only several pixels are available per peak, and the maximum intensity does not necessary represent the true maximum. However, there is a problem that the experimental points cannot be perfectly fitted by Gaussians or by Lorentzians. This is a general problem in TR-LPS spectra, however, in previous applications, where internal calibration has been carried out, this problem has been somewhat canceled out. Nevertheless, we need to perform direct analysis, with no internal calibration, thus this problem must be solved. Thus, the following function has been suggested to fit the actual peaks:

$$y = \frac{A}{1+(e-1)z^{2+\alpha z}} \qquad (1)$$

$$z = \frac{\omega - \omega_0}{\sigma}$$

This function has been shown[41] to reproduce both Gaussians and Lorentzians, therefore has the potential to fill the gap between these two limiting cases. It has 4 fitting parameters, A, ω_0, σ and α. The derivatives of this function can be easily obtained, as need in nonlinear fitting algorithms. (The Levenberg-Marquardt algorithm has been used in this study[42].)

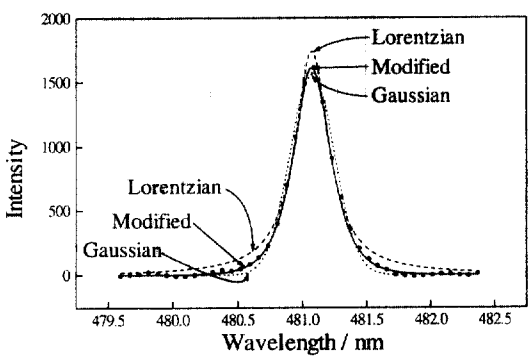

Fig. 2. Several functions used for peak reconstruction

A typical peak reconstruction is shown in Figure 2. This peak, at 481 nm, has been used for analysis of Zn in aerosols. A Lorentzian has been fitted to the experimental points, however, it could not reconstruct the actual shape. It is too high far away from the center. It fits well the points close to the center, however the maximum intensity is many times too high. The fitted Gaussian provided too low points at the sides. Excellent results have been obtained with the modified function described in Equation 1. All peaks have been reconstructed by this function, which provided both the intensity (parameter A) and the area. No significant difference has been observed between performance of calibration plots based on maximum intensity and peak's area, thus, the maximum intensuty (A), has been chosen.

The main problem in aerosol analysis is the large variations of spectra obtained from each laser shot. Figure 1 shows 10 representative spectra obtained from aerosols. These variations are caused by several reasons: First, not every pulse hits an aerosol particle. The concentration of particles might be such that the probability to have a particle in the interaction volume, at the moment of the pulse, is small. On the other hand, it might be that more than one particle is present at the interaction volume. The spectral intensity depends directly on the number of particles in the plasma.

In addition to fluctuations in number of particles in the interaction volume, there are also variations in the mass and size of each particle. Both, mass and size, affect the spectral response. Also the location of the particle in the plasma is of importance. The size of the plasma is in the order of a mm, and the size of an aerosol particle is in the order of a μm. Considering the fact that the temperature in the plasma depends on both time and location, the particular position of the particle, at the instance of measurement, has a considerable spectral effect.

Another factor that should also be considered is variations in the location of the plasma itself: Basically, the plasma is created in air, at the lens focus. However, the actual breakdown can be induced by a small aerosol particle at a different location ahead of the focal point. An additional factor is the screening nature of the analyzed material: Aerosol particles are present in the measurement chamber, and can screen the focal point. In other words, laser light is absorbed by particles before reaching the interaction volume. These particles are far away of the high energy density, and do not

cause plasma formation, nevertheless, they reduce the energy available for the plasma at the focal point. Fluctuations of the laser power also contribute to spectral instability.

The overall result of these factors is that the signals undergo extensive fluctuations. Better results can be obtained under controlled laboratory conditions, however, we are interested here in direct "field" measurements and we have to find a way to partially handle these problems. The first approach is to integrate over many laser shots. This procedure somewhat improves the results, but not significantly. In a previous study we have carried out detailed analysis of the noise in TR-LPS of soils[10], and also found out that extensive averaging cannot improve analytical results beyond a certain limit. The reason is that we are not dealing with normally distributed deviations, and the effects of the above mentioned factors are highly nonlinear. These nonlinearities cause a limited improvement with the number of pulses, much less than $\sqrt{N}$. Therefore, a different approach is needed.

In order to handle the fluctuations, we tested several methods, that are based on rejection of data. The basic idea is to characterize the spectra from single shots and to reject events that are suspected to be anomalous (e.g., no particle present in the interaction volume). The final rejection algorithm provided better results, as compared to a random set of data (including the same number of spectra). Moreover, this algorithm provided better results as compared to the whole set of data (without any rejections). For example, 25 selected spectra provided better analytical results than 100 spectra. The justification of rejection of data is the simple fact that many of the pulses result in irregular (not normally distributed) events. For example, it is useful to reject all spectra originating from events where no particle has entered into the interaction volume. It also makes sense to eliminate spectra from plumes that were produced ahead of the regular focal point, or such that were screened by other particles. The final test of the success of this data rejection process is the analytical performance improvement, as compared to the whole set of data.

The rejection algorithm is based on the following criteria: (a) reject all spectra that have no elemental lines, in addition to the background functional shape. This case might represent absence of a particle in the plasma. Practically, after the baseline has been fitted and subtracted, the intensities at all expected lines are counted, and the spectrum is rejected if their sum does not reach a certain level. (b) reject all spectra where the fitted baseline is too week or too intense as compared to the reference function. The reference function is the average spectrum of clean air plasma. These rejections are considered to represent extraordinary events, where too little energy in available in the plasma, or too much energy is pumped in, due to laser fluctuations. Screening of the focal point by particles, and a "spread" of the plasma along the laser beam, are also represented by this case. This event can be observed as a long bright line, composed of many small sparks along the laser beam. The actual criterion is a factor of 1.5 if the baseline is too weak, and a factor of 2 if it is too intense. (c) the previous criteria usually reject about 30-50% of the pulses. The third criterion rejects all remaining weak spectra, such that only the highest 25% are left. This criterion has nothing to do with the baseline. It is applied to the spectra that passed the first criteria, and their baselines were already subtracted as previously described. This rejection procedure assumes that we can collect as many spectra as we wish, so we can afford analyzing only the most informative ones. Actually, this is usually the case, since 500 spectra can be collected in only 25 s, using a 20Hz laser.

Representative results of the rejection process are shown in Figure 3. Calibration plots for Zn in aerosol, based on the spectral peak at 481.05 nm, are shown. The quality of the calibration plots is deduced from the detection limits. These are calculated from 95% confidence intervals[10]. This definition takes into account both the quality of the calibration line (spread of points), and its slope. The exact procedure for the calculation of 95% confidence detection limits is shown in the inset. It can be seen that the worst results are obtained when the weakest spectra are selected. In this case the standard deviation is high, and the slope of the

line (sensitivity) is low. Only a little better results have been obtained from the same number of spectra, however randomly selected (25% of the actual number of collected spectra). Somewhat better results are obtained when *all* spectra are utilized, without any rejections. Taking into account that this calibration plot is based on 4 times more spectra, the improvement is less than expected. The best results have been obtained with the above mentioned rejection process, that finally ends with ca. 25% of all spectra. It is clearly observed that in this case the standard deviation is the lowest and the sensitivity (slope) is the highest. An improvement of a factor of 3 has been obtained, as compared to utilization of all spectra (without any rejection). An improvement factor of 4 has been obtained as compared to the same number of spectra, randomly selected. This plot demonstrates the usefulness of the proposed rejection procedure.

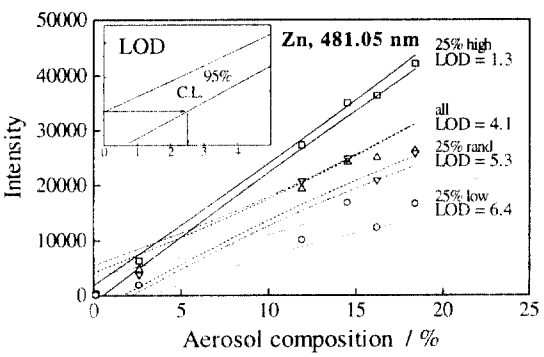

Fig. 3. Calibration plots from various rejection processes.

Similar results have been obtained for other spectral peaks, however, each one produces a different calibration plot. Figure 4 shows 3 such calibration plots for Zn, based on several peaks. The same rejection algorithm has been applied to all these cases. The strong line at 481.05 nm provides better results as compared to other lines. Please note that by using this rejection program, even the worst line, (468.01 nm), provides a better calibration as compared to than the best line when no rejections are applied.

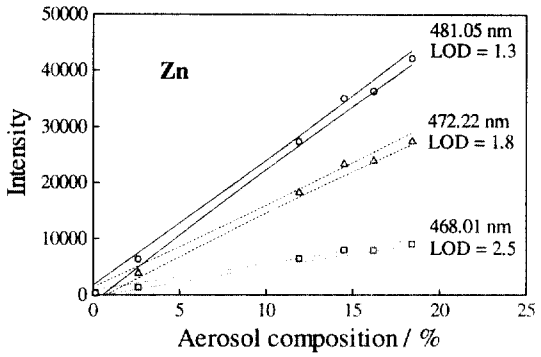

Fig. 4. Calibration plots for Zn, based on various lines, using the rejection program. 95% confidence intervals are shown.

Another important experimental factor that must be taken into consideration is the PDA readout noise. The problem is that when single shot measurements are carried out, the readout noise is added to each single spectrum, while when integrating "on target" (on the PDA) the readout noise in introduced just once[43-44]. When the intensity of each single spectrum is weak, as compared to the saturation limit of the PDA, the readout noise has a considerable contribution that might change the balance and favor the "on target" integration. This is the case when the laser power is not high enough, or the light collection is not efficient. In such cases it makes no sense to collect single shot spectra and the proposed elimination algorithm will probably not provide a considerable improvement. However, when spectra are intense (ca. 10% of the saturation limit), the proposed method offers a considerable advantage. In such cases one cannot integrate too many spectra "on target" anyhow. Thus, in such cases, the advantage of "on target" integration is less important as compared to the loss of information on single events. When good spectra can be collected, it makes sense to apply the proposed rejection method. This method will be even more useful in modern instruments based on intensified CCD, since these devises have a lower dynamic range.

Detection limits of elements in aerosols, by the definition used in this study, are relatively high. It

should be emphasized that these detection limits do not characterize the method, but the actual system under investigation. The natural concentration variations in our particular system were high, thus, the results do not represent the ultimate detection limits of the method. Moreover, better numerical results could be obtained by using more data points, since the 95% confidence interval is much affected by the number of points. Thus, our detection limits should be regarded as representing the analytical performance in this particular system only.

Conclusions

This study has demonstrated the feasibility to partially overcome the problems of spectral fluctuations in TR-LPS of aerosols. Fluctuations originate from the very nature of this method. These are nonlinear fluctuations that cannot be canceled out by averaging over many spectra. The proposed method is based on measurement of spectra from single shots and rejection of irregular events. A rejection algorithm has been proposed. It has been shown that calibration plots were significantly improved by this method, when relatively intense single shot spectra were collected. Both the sensitivity (slope) and the spread of points (standard deviation) are significantly improved. Due to accumulation of readout noise, this method is not expected to work when single spectra are weak (less than a few percentage of the saturation limit). In the particular case currently studied, the method enabled a direct analysis of Zn in aerosols, without any sample preparations. Absolute calibrations (not internal calibration which are based on ratio of concentrations) have been achieved. Detection limits represent only the particular system of current interest, where concentrations changed in the percentage range. Lower limits of detection are expected in other systems.

Further investigation of aerosols from different origins and contamination with lower concentrations, is planned.

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