Analytical note

Quantitative analysis of trace metal ions in ice using laser-induced breakdown spectroscopy

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Abstract

This work reports on a simple, quick-freeze method for the quantitative analysis of trace metal ions in liquids applying the laser-induced breakdown spectroscopy (LIBS) technique. Using this procedure with calibrated samples, well-characterized linear working curves were determined for Na and Al water solutions over the 0.01–1% concentration range. This allowed detection limits of the order of ppm. In addition, optimum experimental conditions were found that allow the analysis to be carried out in a fast and very easy manner, without the limitations and difficulties found with liquid samples. The advantages of this simple and direct method, developed and patented by the Instituto Pluridisciplinar–UCM, are discussed, and potential applications for industrial analysis are also suggested. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Trace metal analysis; Liquid analysis; Laser breakdown spectroscopy

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1. Introduction

The technique of laser-induced breakdown spectroscopy (LIBS) [1,2] provides a simple, fast and direct method of elemental analysis. Indeed, solid, liquid or gaseous materials can be analysed with no, or very little, sample preparation, with detection limits for solid samples in the ppm range. It should be noted that the majority of applications of the LIBS technique have been used for solid samples. In these cases, extensive studies have been carried out under different operating conditions to determine parameters, such as electron density, plasma temperature and spectral line shapes [3,4]. However, much less attention has been paid to the LIBS analysis of liquid samples, due to the fact that a considerable number of alternative analytical techniques with superior sensitivity compared to LIBS are available. Furthermore, plasma generation in liquids presents several problems, for example the strong splashing and sloshing of the liquid produced by the shock waves generated by powerful laser pulses. For high repetition lasers, this behaviour induces a relevant change in the position of the surface with respect to the laser focus, which in turn produces adverse effects in the statistical treatment of the data. In addition, the luminous phase of the plasma is rather short and the spectral lines originating from transitions between high-energy states are severely reduced.

In recent years, an increasing number of studies have appeared on this subject [5–7]. Some of the general findings resulting from these investigations are summarized here. For example, liquids may be analyzed by generating the plasma in the bulk of the sample. This eliminates the splashing phenomenon originated when the plasma is formed on the surface of the liquid [7]. Nevertheless, the major drawbacks of in-bulk analysis are the significant reduction in plasma emission intensity, and the fact that the observation time of the plasma is extremely short, usually of the order of 1 µs or less.

On the other hand, LIBS has been applied to the analysis of liquid samples using laminar flows of the liquid [8–11]. In this case, the detection limits reported were insufficient for the direct application of the technique to environmental samples (pre-enrichment was required). Moreover, the uncertainty in the evaporated volume is very high.

Another approach to overcome the inherent difficulties of LIBS analysis is the technique of double-pulse plasma generation [12–14]. Here, a first laser pulse creates a gas bubble inside the water bulk, while a second laser pulse, delayed in time, analyses the gas inside the bubble. A key drawback of this method is that the liquid needs to be transparent to the first laser pulse, which has to generate the ‘analytical cavities’.

At present, there is considerable interest in the interaction of intense laser radiation with water because of many practical applications, ranging from ablation of biological tissue [15,16] to laser mass spectrometry of organic molecules dissolved in water [17–19].

The present work is dedicated to laser-induced breakdown spectroscopy of frozen water samples and the subsequent analysis of trace elements by emission spectroscopy of the radiant plasma using a TEA-CO$_2$ and a Nd:YAG laser. Given the high versatility of this technique in terms of measurable matrices, it is surprising that frozen aqueous samples have not been given more attention. To the best of our knowledge, routine measurements of real, aqueous, environmental samples have not been yet reported.

This investigation is basically centred on the optimization of detection conditions for Na and Al in frozen water. Thus, well-characterized linear working curves have been determined for the above elements over the 0.01–1% concentration range.

2. Experimental

The experimental set-up, schematically shown in Fig. 1, is similar to that described elsewhere [20,21]. Part of the experiments (measurements with Na solutions) was performed with an infrared Q-switched CO$_2$ laser (Coherent Hull XL-370 TS) operating at a repetition rate of 10 Hz, which could be tuned over the 9–11-µm wavelength range. Experiments with Al-containing
samples were performed with the frequency doubled (532-nm output) of a Nd:YAG pulsed laser (Continuum Surelite I) operated at a frequency of 10 Hz, and characterized by a pulse energy of 200 mJ.

For the analysis of aqueous solutions in their liquid aggregate state, a quick-freeze procedure to generate well-defined slabs of ice was applied. Such solid specimens are much easier to handle than liquid samples, because they largely maintain the inherent homogeneity of a liquid solution.

The water samples were prepared with a volume of 25 ml, which was carefully poured into an inner cup, pre-cooled in liquid nitrogen for 20 s. After 1 min, the water was completely frozen and the sample was again placed into liquid nitrogen for 1 min. The sample was then mounted onto the sample holder coupled to a stepper-motor, which rotated the sample to always present a fresh plane surface to the laser beam.

For the CO₂ laser, a 10-cm-focal-length ZnSe lens was used to focus it onto the sample with an incident angle of 45° with respect to the surface normal. The laser beam was focused onto the surface with a spot diameter of 0.7 mm. The temporal evolution of the laser pulse was monitored using a fast photon-drag detector with a response time of 1 ns (see [22] for details). These measurements gave a full-width at half-maximum (FWHM) value of 100 ns.

The microplasma emission produced after ablation was collected at 90° with respect to the laser propagation direction, using a 1-m optical fibre coupled to an optical multichannel analyser (OMA EG & G 1461/88). The detector consisted of an intensified microchannel plate followed by a 1024-diode array. The detector was triggered by the laser pulse and typically operated with variable delay and gate detection times. The signal was finally stored and processed in a computer for subsequent analysis.

3. Results and discussion

3.1. Qualitative analysis

As a preliminary test, a series of quick-freeze measurements were performed on various reference water samples in order to find the optimum time delay between the laser pulse and the beginning of the LIBS spectra acquisition. Thus, a good compromise between high line intensity and low background signal was obtained using delays of the order of approximately 4 μs after the plasma breakdown. This is evident in Fig. 2, in which the behaviour of one of the Na D-lines

![Fig. 1. Experimental set-up, basically consisting of a CO₂/Nd:YAG laser, a stepper-motor to rotate the sample, a 1-m optical fibre and an optical multichannel analyzer.](image-url)
(λ = 588.99 nm) is represented. Although this procedure has been repeated for all different quick-freeze solutions, no appreciable differences were found in the temporal behaviour of the characteristic LIBS spectra corresponding to different trace elements. Consequently, in order to eliminate the strong plasma radiation, we optimized the data collection using a 5-μs gate after a 4-μs delay. These conditions proved to be adequate for quantitative analysis.

Fig. 3 displays two superimposed low-resolution spectra corresponding to two frozen samples: a common soft drink juice (solid line) and water from the mains in Madrid (thick solid line). The emission lines corresponding to the different trace metals present in the sample are clearly distinguishable above the background. Apart from the line intensities, the close resemblance between the spectra should be noted. The relevant point to be emphasized here is that the overall spectral shape, together with the good signal-to-noise ratio characteristic of different trace elements, makes possible a quantitative analysis of the ‘liquid’ sample (see below). The existence of nitrogen peaks is as a result of working in ambient air.

As an example, Fig. 4 shows a typical LIBS spectrum from an ice sodium solution. The presence of the doublet corresponding to the well-known Na D-lines (2S1/2 ← 2P1/2 and 2S1/2 ← 2P3/2 transitions) is noticeable. The spectrum also reveals the presence of another line of neutral sodium, which corresponds to the 2P1/2 ← 2D3/2 transition.

3.2. Quantitative analysis

It has been shown that, in optically thin conditions, the intensity ratio of a spectral line emitted
by a trace element (denoted by \( i \)) to that emitted by the major constituent (denoted by \( j \)) takes the form [23]:

\[
\frac{I_i}{I_j} = \frac{N_i g_i A_i Z_i \lambda_i}{N_j g_j A_j Z_j \lambda_j} \exp \frac{\Delta W}{kT_e}
\]  

where the energy gap \( \Delta W \) (eV) = \( W_j - W_i \) and the rest of symbols are as follows: \( N \), total population of the species (m\(^{-3}\)); \( g_i \), degeneracy of a given energy state; \( A_i \), Einstein coefficient for spontaneous emission (s\(^{-1}\)); \( Z_i \), partition function; \( \lambda_i \), wavelength of emitted photon (nm); \( W_i \), energy of a given state (eV); \( T_e \), electron temperature (K); and \( k \), Boltzmann's constant (J K\(^{-1}\)).

Applying Eq. (1) to transitions with similar upper state energy, the intensity ratio will only have weak temperature dependence. Taking the natural logarithms in Eq. (1), the following expression can be obtained:

\[
\ln \frac{I_i}{I_j} = \ln \frac{N_i}{N_j} + \ln \frac{g_i A_i Z_i \lambda_i}{g_j A_j Z_j \lambda_j} \frac{\Delta W}{kT_e} 
\]  

(2)

Although \( T_e \) may vary during the acquisition time [24], the overall plasma temperature should not change from sample to sample, since all the experimental parameters, integration time, laser, power, etc., are the same. In addition, with \( \Delta W \) being small, the effect of the last term in Eq. (2) is negligible and not related to the analyte concentration, thus contributing only to the intercept of this straight line, but not to its slope. When the logarithm of the intensity ratio is plotted against the logarithm of the fractional concentration of the trace elements, a straight line, or working curve, is obtained.

Fig. 5 shows the working curve for sodium and aluminium obtained in accordance with Eq. (2) under the present experimental conditions. As in previous work from this laboratory [21], the reference signal was taken to be the background signal. A reference sample was used to confirm that the working parameters (i.e. the distance between the focusing lens and the sample surface) did not change during the experiment. It was always found that the averaged spectral shape and peak intensities, together with the background signal, remained unchanged over more than 100 laser pulses. Note that the linearity of the curve is satisfactory, indicating that the method is, within experimental error, reliable for quantitative analysis. Consequently, the detection limits found from analytical expressions for each working curve were 2 ppm for sodium and 1 ppm for aluminium; these were estimated using the 3\& rule [25]. The major significance of the present results is the clear linearity of the experimentally obtained...
working curves, over the studied concentration range, ensuring their use for quantitative analysis. The observed linearity of the working curve does not mean that the dependence is linear. In fact the experimental dependence for the Na working curve was found to be of the order of 1.31. The deviation of the latter from unity could be due to the well-known matrix effect [23].

The results obtained for a given sample from standard chemical analysis based on atomic emission spectroscopy and LIBS measurements are in very good agreement, as depicted in Fig. 6, where a comparison between both methods is presented. Different Na solutions were measured over the 500–5000-ppm concentration range. The results are plotted and fitted very satisfactorily by a linear $y = ax$ equation, the slope of which was found to be $a = 0.99 \pm 0.02$. The results confirm the linearity and reliability of the LIBS quick-freeze method for precise quantitative analysis of traces in water, up to element concentrations of a few ppm.

4. Conclusions

This work has investigated and proven the feasibility of quantitative analysis of trace elements in frozen water samples using the laser ablation technique coupled to optical multichannel analysis of the resulting microplasma emission. Under this quick-freeze procedure, no splashing occurs on the surface of the liquid and no drastic reduction in plasma emission intensity is observed. Additional advantages of the present technique are: (a) no pre-enrichment of the solution is required; (b) it is much easier to handle than liquid samples, making quantitative analysis with detection limits of the order of a few ppm possible, sufficient for direct application; and (c) neither optical transparency of the liquid nor a sophisticated fiber-coupling procedure arrangement or alignment are necessary.

The present approach easily lends itself to the analysis of real ice and snow samples, e.g. from the Arctic ice cap, to determine trace amounts of various elements in the ice with spatial resolution. This analysis could then be used to link the spatially resolved elemental concentration data to a time scale of environmental influences, provided that quantitative information about the elemental diffusion processes in ice is available.

In conclusion, the present investigation shows that, using the quick-freeze procedure, LIBS is a workable technique for the detection and quantification of trace element in water samples and solutions [26], with superior performance and fewer requirements than liquid-state LIBS analysis.
Fig. 6. Comparison between atomic emission spectroscopy and LIBS methods for analysis of Na concentration. After calibration of both methods, six Na solutions were measured using these two techniques. The results corresponding to the Na line at 588.99 nm were fitted to a linear equation (solid line) with a slope of 0.99 ± 0.02.

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