LASER INDUCED BREAKDOWN SPECTROSCOPY FOR SEMI-QUANTITATIVE ELEMENTAL ANALYSIS IN SOILS AND MARINE SEDIMENTS

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ABSTRACT

The Laser-Induced Breakdown Spectroscopy (LIBS) technique is based upon the analysis of the atomic emission lines generated close to the surface sample. The emission is observed once a laser pulse is focussed on the surface, where the very high field intensity initiates an avalanche ionisation of the sample elements, giving rise to the so-called breakdown effect. Spectral and time-resolved analysis of this emission are suitable to identify atomic species originally present at the sample surface. The method can be certified for analytical applications of interest in environmental monitoring assuming that the surface composition is maintained in the plasma and that ablation processes can be modelled in an appropriate temporal window, assuming quasi-equilibrium conditions. A compact instrument, suitable for both laboratory and field operation, has been designed and tested. Software appropriate for qualitative and semi-quantitative analysis of elements in different soil and sediment matrices has been developed. Calibration free methods for tracing significant pollutant species are under development. Improvements in the laser- induced plasma modelling, based on temperature and electron density measurements aimed at a quantitative determination of some species will be presented and discussed.

INTRODUCTION

Laser-Induced Breakdown Spectroscopy (LIBS) measurements consist of spectral and time-resolved analysis of the atomic and ionic emission lines generated at the surface of a sample after focussing there an intense laser pulse (1-3). Since the early application of LIBS for diagnostic purposes, several systems have been developed for both laboratory (4,5) and field use with portable units (6), taking advantage of its unique characteristics such as quickness, no sample preparation and very low sample consumption, and excellent depth profiling.

In the LIBS technique, the very high field intensity instantaneously evaporates a thin surface layer and initiates an avalanche ionisation of the sample elements, giving rise to the so-called breakdown effect. LIBS spectra can be detected once the plasma continuum emission is almost extinguished. Time- resolved capability is necessary to discriminate the late atomic line emission from the early plasma continuum. High-resolution spectral analysis is required to detect single emission lines, i.e. the spectral signatures of each element. The atomic and in some case ionic lines, once assigned to specific transitions, allow for a qualitative identification of the species present in plasma. Their relative intensities can be used for the quantitative determination of the corresponding elements.

The method can be certified for analytical applications of interest in environmental monitoring, assuming that the surface composition is maintained in the plasma and that the ablation process can be modelled in an appropriate temporal window with quasi-equilibrium conditions. Previous work (7,9) has demonstrated that several different experimental parameters (e.g. laser power and repetition rate, interaction geometry, surface conditions) may affect the effective analytical possibilities of the method, especially if a field application is foreseen which could make a profitable use of its main advantage of no sample pre-treatment needed.

On the other hand, the accuracy of quantitative analysis does depend on the overall sample composition, with a drawback usually known as the matrix effect (1,7). In order to account for deviations in retrieved concentrations due to the matrix effect, a sophisticated modelling of the entire LIBS process, properly including plasma properties and thermal effects, is required for correcting the intensities of detected spectra lines. Our former experiences (8) have shown that, especially in case of laboratory application, matrix effects can be minimised by using of internal standards by calibration with proper reference samples characterised by a similar matrix composition. The approach, however, would limit field experiments to a semi-quantitative analysis in case of highly variable or unknown soil composition.

In this paper the current model utilised in the description of the process is presented together with recent implementations aimed at improving the accuracy for quantitative analysis regarding some elements of environmental interest in soils and sediments of any origin. Significant results obtained on marine sediment collected in Antarctica are reported as an example.

METHODS

Theoretical understanding of some aspects of the plasma generation and heating, such as the laser-sample and the laser-plasma interactions, is crucial for a proper description of the laser ablation process involved. In spite of not straightforward implications on equilibrium, a Boltzmann modelling can be applied to describe the actual state of the plasma triggered by the laser pulse and to reproduce the desired conditions of plasma generation. First let us consider the laser-sample interaction which, under normal working conditions, has the effect to vaporise and atomise a small region of the sample surface, thus resulting in the production of a hot plume consisting of both the ejected material and the atmospheric plasma (3). During this interaction, the laser beam energy is absorbed by the sample and by the generated plasma and several phenomena occur which are responsible for back reflection of the radiation, electron emission, sample heating and phase changes, all affecting the physical properties of the plume in a way peculiar to the sample composition (7).

Once formed, the plasma is usually assumed to reach, in a proper temporal and spatial observation window, a condition of Local Thermodynamic Equilibrium (LTE). In this case, if re-absorption effects are negligible (i.e. the plasma is optically thin), the spectrally integrated line intensity, corresponding to the transition between levels Ek and Ei of the generic atomic species ? with concentration C? , can be expressed as

$$I_a = F.C_a \, \frac{g_k A_{ki} e^{-E_k / K_B T}}{U_a(T)} \tag{1}$$

where T is the plasma temperature, $U_a(T)$ is the partition function, K_B is the Boltzmann constant, and F is a constant depending on experimental conditions. A first order approximation of LIBS measured concentrations can be obtained by comparing a given line intensity from an unknown sample to that from a certified sample (1). Upon the hypothesis of small variation of plasma temperature and concentration, all factors in Eq. (1) are in common except for concentration and line intensity for each element. This allows a simple linear relationship to be established between the specific line intensity and the relevant elemental concentration.

Finally, by observing that the integrated line intensity of Eq. (1) depends linearly, through the constant F, on the plasma density, we conclude that an increase of the accuracy in element concentration measurements can be obtained by using a reference sample with thermal properties as close as possible to those of the unknown sample. If this is the case, including the plasma temperature in the quantitative analysis allows to improve the overall experimental accuracy. By rationing the line intensities originated from the sample and by a reference material (with known elemental concentration), at temperatures T_a and T_r, respectively, we obtain from Eq. (1)

$$\frac{I_a(T_a)}{I_r(T_r)} = \frac{C_a}{C_r} \, \frac{e^{-E_k / k(1/T_a - 1/T_r)}}{U_a(T_a)/U_r(T_r)} \tag{2}$$

Eq. (2) allows to evaluate C_a from the measured LIBS line intensity, while the other parameters are derived from atomic databases at known plasma temperatures. In order to estimate the plasma temperature, from the natural logarithm of Eq. (1) we obtain

$$\ln\left(\frac{I_a}{g_k A_{ki}}\right) = -\frac{E_k}{K_B T} + \ln\left(\frac{C_a F}{U_a(T_a)}\right) \tag{3}$$

In the two-dimensional Boltzmann plane identified by the left hand term of Eq. (4) and by E_k, different emission lines intensities belonging to the same element in the same spectrum lie along a straight line with a slope of $1/K_B T$. If experimental and theoretical data are available for each element in the sample, the combined use of Eq (2) and (3) makes it possible to evaluate the element concentration.

The key conditions for unbiased quantitative LIBS measurements do strongly depend on correctly modelling the process of sample heating. For most material and soils heating is essentially a thermal process, where the mean time between electron collisions is much shorter than the laser pulse duration. We therefore expect the heat rise in the sample to be spatially confined to the laser spot area, with a penetration roughly given by the inverse of the absorption coefficient at the laser wavelength. Therefore, the plasma density (in terms of particles per unit volume), being tightly related to the volume of atomised sample, is strongly dependent upon sample composition. Even in highly conducting metallic samples, heat diffusion can play a role only for long interaction times (at least on the microsecond scale), which is not the case under our experimental conditions. During the plasma observation at LTE the temperature resulting from a Boltzmann plot is typically in the range 7,000 to 9,000K. Under these experimental conditions the contributions of the first ionisation state must be taken into account for the quantitative analyses of the considered element. Unfortunately, for most elements of interest there are no spectral lines belonging to the first ionisation state that are free of superposition in the considered spectral range. In order to estimate the element concentration in the first ionisation state it is necessary to measure the average electron density of plasma during the detection time window. The method here used for calculating the electron density N_e (cm^{-3}) is based on the Saha-Boltzmann equation applied to transitions of Fe and Fe^+ having a sufficiently high number of isolated spectral lines without appreciable self-absorption (2). After calculating the plasma temperature (Eq. 3) and species (atom) concentration (Eq.1) which is proportional to the number of ions in plasma, the electron density is obtained by the formula:

$$N_e = \frac{N_a}{N_i}\frac{U_i(T)}{U_a(T)} B(KT)^{3/2} e^{-\frac{E_\infty}{KT}} \tag{4}$$

where:

- indexes a e i refer to atomic and the first ionisation state, respectively
- E_∞ is the first ionisation energy
- B is a constant with a calculated value of $6.05 \cdot 10^{21}$ cm^{-3}

EXPERIMENTAL APPARATUS

The experimental apparatus used for this work is an improved version of a measurement facility already operating at the ENEA Centre in Frascati and fully described elsewhere (1,8). In this paper it will be shortly reviewed. The third harmonic Nd:YAG pulsed laser beam is driven to the sample surface by a custom-made seven mirror optical arm, especially designed for easy outdoor field LIBS campaigns. The optical arm is terminated by a 250 mm focal length plano-convex lens which focuses the laser beam upon the sample surface. The light emitted by the plasma is collected by suitable receiver optics and carried by an optical-fiber bundle to the entrance slit of a 550 mm monochromator, equipped with three gratings (1,200, 2,400 and 3,600 g/mm) and having a flat focal exit plane of 30 x 15 mm (spherical and chromatic aberration free). At the exit plane, a Multichannel Analyzer based on gated ICCD records the LIBS spectra. All the equipment is controlled by custom-written software routines, working in a Windows 95/98 environment. Initially, great care has been devoted to operate the system under reproducible conditions at constant laser energy, but after introducing spectra normalisation as well as plasma temperature and electron density calculations the quantitative measurements resulted almost independent of laser energy if maintained constant during the acquisition of one set of spectra.

The investigated sample, mechanically compacted by a press and inserted on a rotating holder, is constantly rotated in order to minimise crater effects and to partially compensate local inhomogeneities. The holder design ensures a constant distance of the surface sample from the lens. Sample movement, number of laser shots, and other experimental parameters were adjusted to optimise the measurement reproducibility (9). The current set-up characteristics are summarised in Table 1.

Table 1: LIBS system specifications

Transmitter		**Detection unit**	
Laser Nd:YAG	**Quanta System**	**ICCD**	**ANDOR**
3rd harmonic @355 nm		Pixel size	25 µm
with unstable resonator		active pixels	690x 256
Energy	5-30 mJ	Dynamic Range	18 bits
pulse width	8 ns	Spectral range	180 - 550 nm
prr	10 Hz	Phosphor	P43
Receiver optic		**Control unit**	
Fiber optic coupling	**ORIEL**	PC	Pentium 166MHz
F#	4	BUS Control	IEEE 488
size	100 µm	SW	LabView
bundles	16		
Mobile arm	**EL.EN.**	**Performances**	
mirrors	7	Typical resolution	9000 $\Delta\lambda/\lambda$
focal length	25 cm	Acquisition time	3 min
Monochromator	**ISA Jobin-Yvon**	Elaboration time	5 min
fully computer controlled	TRIAX 550		
Lenght	550 mm		
Triple grate turret	1200-2400-3600 gr/mm		
F#	6.4		
Slit	10 - 100 µm		

RESULTS AND DISCUSSION

Qualitative analysis

Eq. (1) and (2) show a relation between line intensity as measured by a LIBS apparatus, concentration of elements present in the sample, and spectroscopic data usually found in literature.

To be able to use the compact design of the LIBS apparatus in field operation, easiness of use is very important. Therefore, one of the goals was to develop a software able to perform a fully automatic qualitative analysis. Basically, the software consists of two modules (see also the flowchart in Figure 1):

1. A LabView module that contains the graphical user-interface and performs the pre-processing and fitting of the LIBS spectra. The output is a calibrated and fitted LIBS spectrum.
2. A C++ module that compares the calibrated and fitted LIBS spectrum with a spectral database of literature values to find which elements are present in the LIBS spectrum. By comparing the peak intensities of identified peaks with reference files that have been analysed in the same way before, an estimate can be given of the concentrations involved.

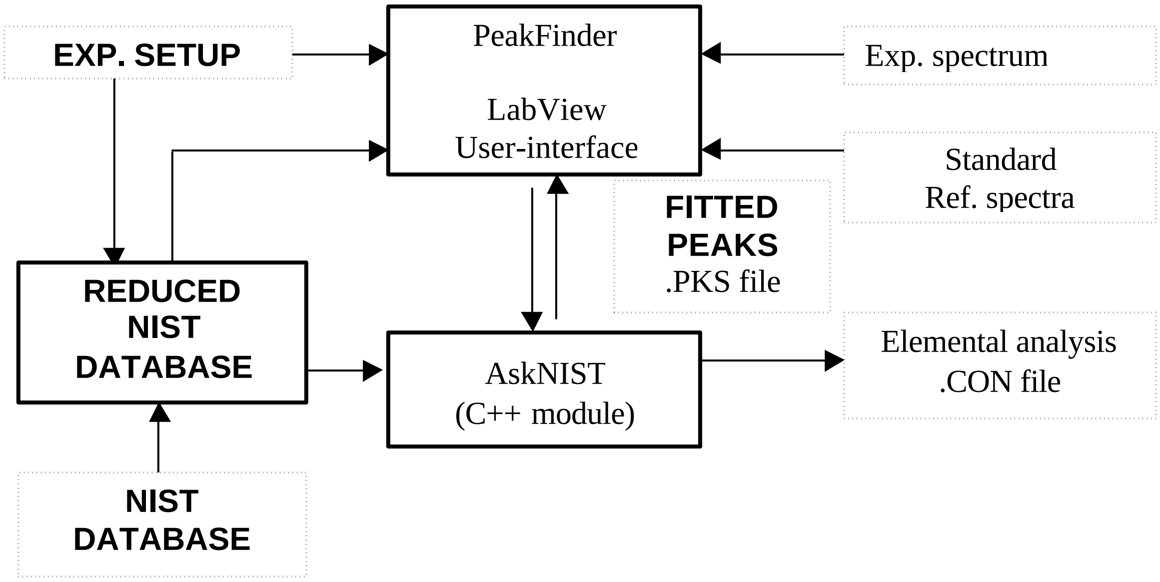

Figure 1: Flow-chart of the software for qualitative analysis. The LabView module does acquisition and pre-processing of experimental data. An external module written in C++ assigns the right atomic elements to the fitted peaks. Only those peaks with only one element assigned will be used for qualitative analysis.

Unfortunately, due to the complexity of the LIBS spectra, the present version of the automatic peak fitting is not working at optimum in the identification of weak spectral features and in the deconvolution of multiplets. Although we are still working on its improvement, results are already satisfactory for field operation on most elements when a sensitivity below the ppm level is not pursued.

For the assignment of the fitted peaks to each element in principle we have to consider the presence of all the others except for the lighter ones. This makes it very difficult for the program to automatically assign the right elements without any human supervision. By cross-checking with a spectral database of literature values, by giving more importance to the stronger lines, and by checking the expected number of lines for a specific atomic element with the number actually found, a decision table is built, which allows for as much erroneously assigned elements as possible to be removed. At the end, mostly on the basis of the assignment of peaks with 100% certainty, a decision is made on the presence of a specific atomic element. By comparing these peaks with the same peaks of a reference measured sample dispersed in a similar kind of matrix, we can get an indication of the concentration of this atomic element (see Eq. (2)).

Quantitative analysis

In practical situations, calibration curves can be built in the way described above according to Eq.(2). The approach has proven to be valid for retrieving the concentration of a single species and in a well-defined matrix (8), while the procedure appears inappropriate in complex cases, such as multi-elemental analysis or when any *a priori* knowledge of the sample (i.e. of the rough matrix composition) is lacking.

In order to reduce matrix effect as well as the uncertainty due to long-term laser instabilities on quantitative analyses, we applied a procedure of normalisation of LIBS spectra against the integrated plasma intensity (10) collected by the instrument in the investigated spectral range. Before fitting emission lines as described above, each spectra was corrected for the overall instrument response as a function of wavelength, which was previously measured by using a lamp characterised by a calibrated spectral irradiance.

It was assumed that the correction factor F from equation (1) is not the same for all elements and initially was settled to value 1 for iron concentration (Fe + Fe$^+$). After temperature and electron density calculations for each spectra of a chosen reference sample, we determine the average concentration of neutral atoms and the program automatically performs a calculation of first ionisation state concentration and of the total element concentration. Ionisation states above the first have not be taken into account. The concentration of atoms utilised was the average value obtained for lines free of overlap or with overlap with weak lines of minor elements. The lines chosen for concentration calculation all belong to the reference line database (11) completed by line data from the Kurucz database (12).

By using certified concentration values of reference samples with different matrix types, calibration curves were created for each element under investigation.

Spectra normalisation by integral plasma emission significantly reduced the matrix influence on quantitative analyses, and for some elements (e.g. Cr, Cu, Ni) the scattering around the calibration curve corresponds to an error lower than 30% even for a concentration range covering three orders of magnitude.

Unknown samples were treated as described above, except that corresponding element concentration, considering atoms and the first ionisation stage, were determined from the calibration curves adopted (Figure 2).

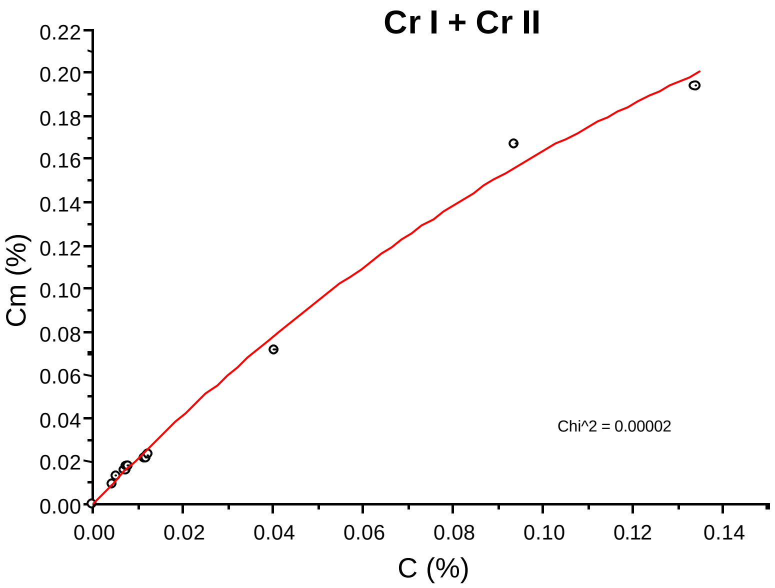

Figure 2: Calibration plot – measured concentration of chromium (Cr + Cr$^+$) as a function of certified concentration for different matrix type samples.

Discussion

LIBS experiments have been carried out on some soil samples with representative contents in chromium, lead and zinc, and other investigated elements. The reference soils are from several international institutes for Reference Material and Standard (IRMM CE, NBS USA, SOSMT Slovak Republic). A 25 cm long core of Antarctic sediments collected during the XIII Campaign has been examined in comparison to a standard certified sample MURST-ISS-A1 from a former mission (XI), sediment layers were selected with a height of two centimetres. The resulting element concentration obtained by LIBS technique, both on certified and unknown samples are given in the following Table 2. A good agreement is found between the certified concentration values and those ones measured by LIBS. In the unknown sample most of the elements showed a rather uniform distribution through the sediment layers, while the same examples of less uniform distribution are given in Figures 3 and 4 for titanium and barium, respectively. A few elements were also determined by ICP in the unknown Antarctic sample, flat distributions were measured in all cases. LIBS and ICP results (here given in parentheses) were found in agreement with the statistics for iron (1.7 ± 0.2 %), copper (37 ± 10 ppm), and manganese (575 ± 100 ppm).

Table 2: Measured element concentration of certified Antarctic sample and of different sediment layers from unknown Antarctic sample. In sample MURST-ISS-A1 elements marked with (*) are not certified.

Element	Unit	MURST-ISS-A1		Antarctic sediments with medium layer depth given below								
		Certified	Measured	Medium value	Error (%)	1 cm	3 cm	5 cm	9 cm	13 cm	19 cm	22.5 cm
Fe	%	2.44 ± 0.07	2.09 ± 0.42	1.44	20	1.37	0.94	1.04	1.27	1.24	1.27	1.69
Al	%	6.71 ± 0.33	4.98 ± 1.74	2.05	35	1.94	1.50	1.82	2.30	2.10	2.32	2.35
Na	%	1.97 ± 0.11*	1.48 ± 0.52	1.30	35	0.74	0.67	1.25	2.25	2.47	0.83	0.86
Mg	%	1.52 ± 0.13*	1.34 ± 0.33	0.61	25	0.43	0.92	0.67	0.63	0.67	0.50	0.47
Ca	%	1.58 ± 0.17*	1.68 ± 0.42	3.1	25	3.95	3.47	2.58	3.14	4.18	2.32	2.04
Mn	ppm	446 ± 18	424 ± 106	513	25	588	498	454	349	734	839	546
Cr	ppm	42.1 ± 3.4	42.8 ± 10.7	57.1	25	71.8	71.8	59.9	45.1	56.0	32.6	62.6
Cu	ppm	5.79 ± 1.59*	-	20.5	30	22.1	14.2	24.4	35.2	19.0	12.1	16.4
Ni	ppm	9.56 ± 0.04	10.7± 2.7	19	25	18.4	20.0	19.7	28.0	18.7	13.0	15.5
Ba	ppm	464 ± 61*	467± 131	243	30	197	82	260	205	316	375	266
Ti	ppm	*	529± 159	248	30	124	227	139	156	345	389	359
Zn	ppm	53.3± 2.7	87± 35	195	40	158	111	98	352	125	246	276

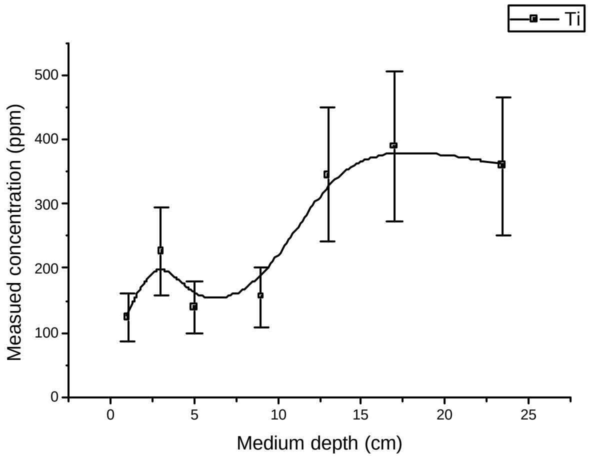

Figure 3: Titanium distribution through the Antarctic sediment layers

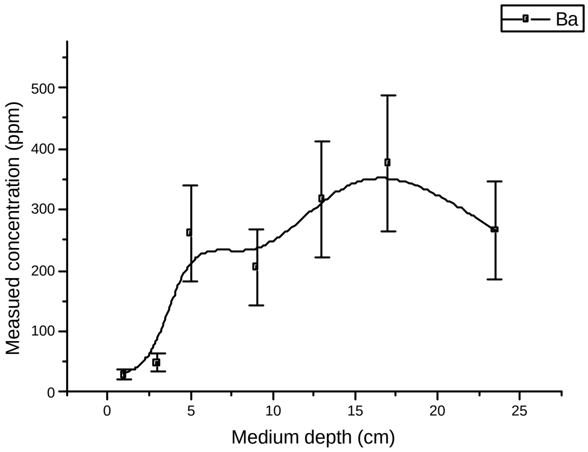

Figure 4: Barium distribution through the Antarctic sediment layers

CONCLUSIONS.

The results of the present study demonstrate a significant reduction of the matrix effect on quantitative soil analyses as well as the influence of laser pulse energy from one spectral acquisition to another. By applying spectra normalisation and plasma modelling, after first generating calibrating curves for each element and for a given experimental set-up, concentration measurements of unknown samples independently of their matrix composition, could be determined with an error lower than 40%, and for some elements even within an error of 20%.

A comparison of the present results with others obtained in soil samples, shows that the LIBS technique described here promises on-line soil analyses of various elements, without any further calibration and without sample preparation. By this technique element concentrations are measured within reasonable error bars, over a range covering several orders of magnitude that could be further reduced. In our quantitative analyses of soil samples, the major contribution to the overall error is attributed to the fitting of emission lines, which also causes errors in plasma temperature and electron density calculation, and finally in determining the single element concentration. Further development should also improve the algorithm for self-spectra calibration that is particularly critical for concentration measuring of elements with weak and very few spectral lines free of overlapping. Calibration curves should be enriched examining other certified samples with element concentration covering the specific ranges of interest.

ACKNOWLEDGEMENTS

The present work has been partially funded by the Italian Ministry of Environment (Commessa PR/12E) and by the National Programme of Research in Antarctica

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