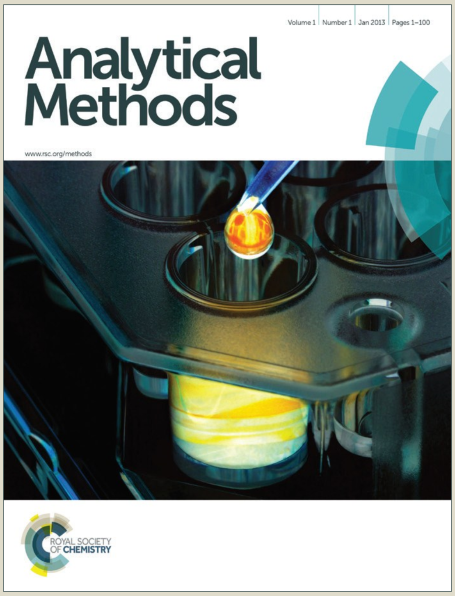

Analytical Methods

PAPER

Mechanization of Measurement of Laser Induced Breakdown Spectroscopy/Ring-Oven Pre-Concentration: Determination of Copper in Cachaça

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/methods

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The hyphenation of the micro-analytical sensing characteristics of LIBS with the ring-oven pre-concentration capability results in better detectability for that spectrophotometric technique, as has been recently demonstrated. However, the system described previously was heavily dependent on operator skills to fire the laser shots onto the ring perimeter, a slow procedure that limits the number of laser pulses that can be integrated to achieve better signal-to-noise ratio. This drawback is overcomed in this present work by allying a mechanical spinning device and an internal standard (Li) to permit reproducible and operator free measurement of the ring contents by LIBS. The system was evaluated and employed to develop a new analytical method aiming to determine copper in cachaça®, a Brazilian spirit made of sugar cane juice. The internal reference was conceived to correct for most of the variables affecting the precision of the analytical signal due sample matrix variation, ring making, and measurement by LIBS. Sample volumes of spirits as low as 60 µL can, after pre-concentration by ring-oven (pre-concentration factor = 15), yield a detection limit of 0.3 mg L^{-1} of copper and average absolute errors, when compared with results obtained by the atomic absorption reference method, of 0.5 mgL^{-1}.

1. Introduction

Laser induced breakdown spectroscopy (LIBS) is reaching the maturation stage among the modern techniques of chemical analysis. The fundamentals and majority of practical aspects of the technique have been reviewed throughout the last decade [1-3]. The mostly distinguished features of LIBS are associated with its fast, quasi non-destructive, direct and multi-elemental micro analytical characteristics. In fact, the technique produces almost instantaneous analytical information by firing and focusing a pulsed laser beam on a minute spot (often smaller than 100 µm diameter) of the sample surface [4]. Lateral and depth spatial resolution are easily achieved [5-7].

Despite the efforts to extend the scope of LIBS to samples in all physical state (gaseous, liquid and solid), the success of the technique has been undoubtedly attested only for solid samples. The difficulties with liquid samples arises from loosing of laser pulse energy to volatilize sample solvent, resulting in lower energy for sample ablation and excitation, and from changes in the liquid surface following the incidence of the laser pulses. All together, these problems reduces the reproducibility and detectability of the LIBS based analytical methods applied to liquid samples[8,9].

To overcome the problems of direct analysis of liquids by LIBS, the transference of the sample to a solid substrate has been often proposed [10-15]. This transference can overcome most of the drawbacks associated with the direct measurement of liquids by LIBS. After the transference, the solid substrate contains the analytes and the method evolves as for a solid sample. However, the transference to a solid substrate usually works against the detectability of LIBS by dispersing and diluting the sample in the solid substrate. Therefore, if low detection limits are necessary the transference must be accompanied by a pre-concentration in the solid substrate. The literature describes several approaches to obtain the transference of the analyte from the liquid sample to a number of solid substrates, such as wood, paper, graphite, etc. [10-13]. Some of the methods employ a simultaneous concentration of the analyte over the solid substrate [14-15].

Recently, the classical ring-oven technique has been revisited with the same objective of analyte transference from a liquid to a solid (filter

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See DOI: 10.1039/x0xx00000x

paper) substrate with simultaneous pre-concentration, followed by measurement using LIBS [16]. The ring-oven was invented by Weisz in the 1960's, and employed as a micro analytical, mainly qualitative, technique of pre-concentration [17]. The ring-oven presents some useful characteristics regarding its use in the analyte transference intended for LIBS quantification. The technique is based on delivering a small volume of liquid sample to the centre of a filter paper disc placed in a small circular heated (to about 120 °C) oven (the ring-oven) where it diffuses by capillarity and evaporates after reaching a certain distance from the centre of the disc. The added sample is washed by additional increments of discrete volumes of sample or by a suitable washing solution that transport the analytes, depositing the non-volatile species in a tinny circular region (the ring). Pre-concentration factors can be over 200 times for sample volumes as low as 600 μL, and the technique employs no hazardous solvents or special adsorbing materials besides common filter paper.

The LIBS and the ring-oven techniques couple synergically because LIBS is benefitted by the analyte transference to a solid and overall invariant prevalent matrix substrate (filter paper) while ring-oven provides the pre-concentration required for LIBS to achieve better detection limits. The LIBS micro-analytical characteristic is also used to advantage, permitting direct probe of the minute region (about 200 – 300 μm wide) of the ring by the focused laser pulse.

Although the principles and advantages of hyphenating LIBS and ring-oven has been previously demonstrated [16], the original approach employed a manual measurement of the ring, acquiring and averaging up to sixty LIBS spectra by targeting the probing laser pulse into the ring, using the naked eye supported by a visible (red, 660 nm) laser pointer to target each laser pulse. The measurement operation is, therefore, cumbersome and time consuming. Furthermore, no correction for pulses missing the ring target was provided.

This work proposes a mechanical device to assist in the ring measurement by LIBS and suggest the way to overcome the effect of missing laser pulses and several other factors affecting the ring-oven technique, by employing an internal standard. To demonstrate the usefulness of the proposed approach, the pre-concentration method by ring-oven and the LIBS mechanized measurement system were employed to determine copper in cachaça®, a Brazilian spirit resulting from fermented sugar cane juice, containing from 38 to 48% (v/v) ethanol.

Brazilian official regulatory institutions establish limits for copper content in cachaça of 2 or 5 mg L^{-1}, for exportation or in-country consumption, respectively. The metal contaminating cachaças originates from the vessels (called "alambiques") employed to distil the fermented sugar cane juice, which must be made of metallic copper, to impart the desirable organoleptic characteristics to the spirit. Of course, attack of the metal surface can produce substances, such as the basic copper carbonate, which can be carried into the condensed product during distillation. The presence of copper beyond the allowed limit can irreversibly affect the neural, hepatic and renal human systems at long term. Several other metallic contaminants can be found in cachaça. However, besides copper, only lead is regulated, and should be present under 0.2 mg L^{-1} in cachaça.

2. Experimental

2.1. *Samples, standards and reagents*

Eight unsweetened cachaça (the most common type) samples produced in different regions of Brazil were acquired in the local commerce. The ethanol content of the samples varied from 38 to 48%. All reagents were of analytical grade. Standard reference solutions of copper (Fluka) and lithium (Furlab) were employed. Surrogate cachaça standards, containing copper in different concentrations (typically from 0.0 to 8.0 mg L^{-1}), were prepared by suitable dilution of the stock reference solutions to contain also 2.0 mg L^{-1} of Li and 42% (v/v) ethanol to approximately match the average alcohol content of the cachaça samples. The washing solution was prepared to contain 38% (v/v) ethanol and 0.05 mol L^{-1} HCl. Analytical grade reagents and deionized water were used throughout.

2.2. *Laser induced breakdown spectroscopic (LIBS) system*

The LIBS system employed is very similar to that previously described elsewhere [16]. The modifications refer to the use of a mechanized sample measurement device, which is described in detail below, and to the analytical signal acquisition mode. In this case, the software driven the data acquisition by the ICCD (Intensified Charge-Coupled Device) camera coupled to the echelle polychromator was programed to integrate the number of pulses delivered to the ring during a time window (t_w) of 6 s.

The relevant characteristics of the LIBS instrument employed are: Nd:YAG laser producing radiation pulses at 1064 nm, pulse duration of 5.5 ns, pulse rate 20 Hz, pulse energy of 100 mJ (nominal) and 90 mJ (actual), beam diameter of 5 mm, yielding an estimate irradiance at the lens focusing point equal to 1.3 x 10^{12} W cm^{-2}. The lens has a focusing distance of 10.0 cm. However, to avoid air breakdown, the sample is positioned at a distance of 9.7 cm from the lens.

The device proposed to mechanize the measurement of pre-concentrated samples by ring-oven employing LIBS is very simple and is depicted in Fig. 1a. The device is constituted of an x-y-z linear positioning devices, supporting a dc motor (12 V, 5000 rpm) coupled to a reduction gearbox. A spinning platform made of PTFE is coupled to the axis of the reduction box. The filter paper disc, containing the ring produced by the pre-concentration procedure, is placed on this platform. An external cap, also made of PTFE, is employed to hold the filter paper disc flat in place. Details of the rotating platform (removed from the gearbox axis) can be observed in Fig. 1b. As shown, the PTFE disc, coupled to the gearbox axis, has a central needle used to guide the filter paper disc in order its previous marked centre coincide with the platform centre. The rotation speed is set by a potentiometer controlling the potential difference applied to the dc motor from 0 to 12 V. The usual rotation speed employed was 10 rotations per minute. The arrangement is placed below the focusing lens of the laser pulse, which impinges perpendicularly into the filter paper surface. The system is positioned using the x-y linear positioning devices and a red laser pointer (not shown in Figure 1a) marking the local previously determined where the LIBS laser pulses are focused. When the ring region is at the red laser spot, the motor is turned on. In combination with the LIBS system described before and the time window (6 s) employed for integrating the emitted radiation, 120 pulses are sampled per each turn of the platform. A complete measurement of the sample can be completed in about 1 min, including sample presentation and removal.

2.3. *Ring-oven system and pre-concentration procedure*

The ring-oven system is similar to the one described elsewhere [16]. The system comprises a Flow Injection (FI) manifold used to manage sample and washing solutions, and the oven, made of aluminum cylinder, supplied with a collar like resistive heater. The FI system is constituted by a peristaltic pump, and a proportional sample injection valve. In the present case, a fixed and reproducible volume of sample is defined by a segment (loop) of small bore PTFE (Polytetrafluoroethylene) tubing (0.80 mm, inner diameter) fitted in the proportional injection valve. The typical volume of sample employed is 60 µL. Sample volume can be easily altered by changing the length of the PTFE tubing.

The pre-concentration of a sample commences by placing a filter paper disc (3.0 cm diameter, Whatman 40), previously stained in its center by 10 µL of an ethanolic solution containing 0.005 % (w/v) of cresol red. This dye will serve to locate the ring profile on the paper disc after the pre-concentration has been accomplished. Typically, the sample solution is always previously spiked (using a stock standard solution containing 1000 mg L^{-1} of lithium) to produce a fixed 2.0 mg L^{-1} lithium concentration in the samples and/or standards solutions employed for construction of analytical curves. The sample present in the PTFE loop is carried by an air stream flowing at 25 µL min^{-1} to the ring-oven, where it is delivered drop-to-drop to the center of the paper disc. Oven temperature was kept at (110.0 ± 0.2) ^{o}C. After sample delivering, a suitable volume of the washing solution (typically 45 µL) is inserted into the FI system and delivered to the ring-oven. The flow rate of the solutions was stipulated to allow the delivered drop of liquid to diffuse to the very frontier possible to be reached by capillarity, and drying of the solvent, before the next drop is released on the filter paper. The total time required for a typical pre-concentration is about 6 min. The oven diameter (2.5 cm) was designed to avoid the diffused liquid to reach the oven wall. Typical diameter of the ring formed after pre-concentration is 1.90 cm.

The LIBS system has been optimized for the delay time, integration time and gain of the photoelectrons multiplier of the ICCD camera by employing filter papers stained with 20 µL of a stock solution containing 1000 mg L^{-1} of copper. The stains permits the optimization of the LIBS system using the same matrix (filter paper), but in the absence of any factors affecting the repeatability of the LIBS signal associated with the ring-oven pre-concentration procedure. The best conditions found considering the highest signal to background and signal to noise ratios were: delay time and integration time per laser pulse of 1 µs, and photomultiplier gain of 100.

Surrogated cachaça samples prepared to contain 42% (v/v) of ethanol, 3 mg L^{-1} of Cu, and spiked with 2 mg L^{-1} of lithium were employed to verify the efficiency of the ring oven pre-concentration system. Initially, it was investigated the volume of washing solution required to quantitatively carry the analyte and the internal standard present in 60 µL of sample towards the ring. The washing solution was prepared to contain 38% (v/v) of ethanol and 0.05 mol L^{-1} of HCl. 45 µL of this solution can effectively wash the Cu and Li delivered by the sample to the filter paper in the ring-oven system, as can be observed in Fig. 2.

The pre-concentration factor was estimated as previously described [16]. For a pre-concentrated volume of 60 µL the factor was 15. For comparison purpose, if 20 µL of a standard copper solution containing 241 mg L^{-1} is delivered to a filter paper, and measured by LIBS, its analytical signal matches that obtained by pre-concentrating 60 µL of a solution containing only 5 mg L^{-1} using the ring-oven system.

2.4. Determination of copper in cachaça by the reference method

The cachaça samples were analyzed by their copper content using the standard method recommended by Adolfo Lutz Institute, Brazil [18], based on flame atomic absorption spectrometry (FAAS) and standard addition method to correct for ethanol content variations among samples. The ethanol content affects the viscosity of the solutions and, consequently, the nebulization process, changing significantly the analytical signal. The determinations were made in triplicate and the absorption measurements performed at 324.7 nm in a Perkin-Elmer Atomic Absorption spectrophotometer (AAnalyst 400) employing an air (10.0 L min^{-1}) / acetylene (2.5 L min^{-1}) flame.

3. Results and Discussion

3.1. Evaluation of the efficacy of the internal standard (Li)

Lithium is employed as internal standard for the determination of Cu in cachaça to overcome or minimize several factors affecting the repeatability of the analytical signal. Any variation in the ring-oven pre-concentration parameters, such as the oven temperature, sample matrix, and sample deliver rate can potentially alter the ring diameter, consequently the pre-concentration factors, and the absolute LIBS signal intensity.

Other relevant factor is the number of laser pulses missing the ring region during measurement by LIBS. Because the circle formed by the ring-oven system is not perfect, whereas the sequentially fired laser pulses tracks a perfect circle on the filter paper, as demarked by the mechanized measurement device, it is possible that some pulses total or partially fail reaching the ring. This is also a source of variability of the integrated LIBS emission signal, which can be corrected by taken the ratio of emissions.

Finally, the internal standard can correct for variations of the sample volume effectively delivered to the ring-oven system, because the ratio of LIBS signal is related only to the ratio of Cu and Li contents, the last one maintained constant.

Fig. 3 shows analytical curves obtained by pre-concentrating 60 µL of surrogate cachaça samples whose Cu content is in the range 0 - 8 mg L^{-1}. The error bars (the estimated standard deviation for three rings) over the mean analytical signals are remarkable lower for the analytical curve obtained by employing the intensities ratio (Cu/Li) than they are for the absolute intensities for Cu. The results for the higher (8 mg L^{-1}) concentration of Cu may have been affected by the ring preparation and shows lower precision. Anyway, the gain in using the internal standard can be observed yet.

Note that the selected internal standard is not appropriate to correct for fluctuations directly associated to the LIBS parameters, such as the laser pulse energy, because the energy associated to the wavelength radiation emitted by Cu and Li are too much different. On the other hand, Li is a metal rarely found in cachaça, which is an essential characteristic of any internal standard.

3.2. Effect of sugar content

Cachaças containing very low amounts or no sugar are the most commercialized and valorized products. However, several low quality products may contain up to 20% (w/v) of added sugar.

To investigate the effect of sugar content on the proposed method, five series of standards containing copper in the range 0 - 8 mg L^{-1} and 0, 2, 5, 10, and 30 % (w/v) of sucrose were prepared and 60 µL of those solutions where pre-concentrated by ring-oven, generating 5 analytical curves. Lithium was employed as internal standard at level of 2.0 mg L^{-1}. The analytical signal was taken as the ratio between the Cu and Li emission intensities.

It was observed that by adding 2% (w/v) of sugar causes a decrease of the slope of the analytical curve (0.06556 to 0.04373 L mg^{-1}) when compared to that prepared by standards containing no sugar. For larger contents of sugar (2 to 30%), the slopes are quite constant varying from 0.04373 to 0.04739 L mg^{-1}. However, the precision of the analytical signals is degraded at larger sugar contents, because this species also pre-concentrates in the ring, causing a substantial change in its final composition and on the ring format.

3.3. Effect of the sample volume pre-concentrated

The ring-oven system can achieve greater pre-concentration factors by using larger volumes of sample. Gains exceeding 3.5 times in the slope of the analytical curve for Cu was observed by pre-concentrating 300 μL of solution instead of 60 μL. Fig. 4 show the analytical curves obtained and the relevant fitting parameters. To perform this evaluation, the Cu concentration need to be reduced to a maximum of 1.5 mg L^{-1}, and the amount of Li added as internal standard was varied according to the pre-concentrated volume to achieve a similar concentration in the ring as produced by a 2 mg L^{-1}, when 60 μL of solution is employed. The reduction of concentration was necessary to keep the analytical curve for higher pre-concentrated volumes within the linear region. Increasing the pre-concentrate volume is a convenient way to increase the detectability of the ring-oven/mechanized LIBS system.

3.4. Figures of merit for the proposed analytical method

The repeatability of the ring-oven/mechanized LIBS measurement method was evaluated by determining the Cu content of three samples of cachaça by the standard addition reference method and by the proposed method based on the ring-oven pre-concentration and mechanized LIBS measurement. Table 1 shows that the repeatability obtained by the proposed method, though always worse, compares well with that achieved by the standard addition reference method and can provide the necessary performance to determine Cu in cachaça.

The accuracy of the proposed method was evaluated by determining the Cu content in eight samples of unsweet cachaça. Table 2 shows that the results are comparable to the reference method based on standard addition. In fact, no significant difference was detected at 95% confidence level after a statistical test (test *t*) is applied to the data. In that table, a significant difference was observed for sample 6. This sample may contain sugar in an amount that can decrease significantly the analytical signal, as observed during the study of the effect of sugar content on the LIBS analytical signal.

The detection (LOD) and quantification (LOQ) limits were evaluated by using 3 and 10 times the ratio of the standard deviation of the blank and the slope of the analytical curve. The standard deviation of the blank was estimated by measuring ten replicates of rings prepared from 60 μL of a standard solution prepared to contain no Cu but with 2 mg L^{-1} of Li. The limits of detection and determination were 0.3 and 1.0 mg L^{-1}, respectively.

3.5. Stability of the analytical signals

One of the advantages of the ring-oven pre-concentration method is that the rings formed on the filter paper can be stored and transported to be measured in a laboratory distant from the sample pre-processing local. However, during the development of the present work, it was observed that the analytical curves change their parameters (slope and intercept) from day to day. Therefore, two experiments were designed to find the causes of this variability. The first one consisted in to produce four series of rings, required to construct four analytical curves for Cu content from 0 to 8 mg L^{-1}. All standards also contain Li at 2.0 mg L^{-1}. The rings were produced in the same day and stored. Each series was measured by the mechanized LIBS system every week, during one month. The results show a significant variability in the slope of the analytical curves, with a maximum relative difference of 19%. In the second experiment, the rings required to make the analytical curve was prepared and measured in the same day. In this case, five analytical curves were obtained. The maximum relative difference in the slope was 23%. These results permits to conclude that the main source of variability is caused by fluctuation in the LIBS instrument. Therefore, it is recommended the determination of Cu in cachaça be made by taken all measurements (those to construct the analytical curve and those of the samples) in the same day. Furthermore, the advantage of storing and transporting the filter papers containing the rings was demonstrated by the results of the first experiment, at least for those rings stored for a period of one month.

The fluctuations of the LIBS system parameters, mainly associated with the laser pulse energy, alter significantly the ratio of the intensities between the analyte (Cu) and the internal standard (Li) because, as mentioned before, this type of variation does not affect the analyte and internal standard signals in the same proportion. This causes the variability of slope of the analytical curves obtained during successive days.

3.6. *Detection of low concentration contaminants in cachaça*

Lead is a cachaça contaminant whose content should be below 0.2 mg L^{-1} [19]. Although this work did not aim to quantify the content of Pb, some preliminary experiments were carried out to demonstrate the potential of the proposed method to screening or even determine this species in this spirit.

The LIBS signal showed in Fig. 5 was obtained for a surrogate sample containing 0.20 mg L^{-1} of Pb by increasing the pre-concentrated volume to 1500 μL and replacing the washing solution by a 38% (v/v) ethanol containing 0.05 mol L^{-1} of acetic acid (to avoid precipitation of $PbCl_2$). As can be noticed, the detection of Pb in the surrogate sample, containing Pb at the allowable limit, was achieved, demonstrating that the method can be used, at least, to screen samples for the presence of the contaminant.

4. Conclusions

In this work, the ring-oven/LIBS technique has been improved by including a mechanized device to reduce about ten times the measurement time of the rings containing the pre-concentrated analyte by LIBS, and by the use of an internal standard at fixed concentration to avoid or minimize the effect of several sources of imprecision affecting the analytical signal.

By computing the analytical signal as the ratio of intensities between the analyte and internal standard signals, the effects of sources of imprecision of the ring-oven/LIBS technique (laser pulses missing the ring target, fluctuations in the pre-concentrated sample volume, and several factors associated with the sample matrix) can be minimized.

The selected internal standard (Li) can help to overcome several problems associated with the repeatability and detectability of the ring-oven/LIBS technique. However, it is not suitable to correct for the fluctuations in the LIBS parameters, such as the pulse laser energy. Consequently, the analytical performance of the ring-oven/LIBS method for the determination of copper in cachaça is not superior to that of the reference method. However, the performance is enough to analyse this type of sample and to attest its quality. The technique can be adapted to determine or to screen samples for other contaminants, such as Pb.

The ring-oven technique provides a unique characteristic permitting the rings produced on filter papers to be stored, and transported to a distant laboratory for measurement.

Further applications of the mechanised ring-oven/LIBS system can be foreseen in the field of environmental interest and residues of metals in wastewaters.

Acknowledgements

This is a contribution of the INCTAA (FAPESP, proc. no. 2008/ 57808-1 and CNPq, proc. no. 573894/2008-6). B.B.F.F. is grateful to CAPES for the PhD fellowship.

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Figure Captions

Figure 1. (a) Laser induced breakdown spectroscopic system and the mechanized device developed for ring oven measurement. (b) Detail of the spinning platform and cap with the filter paper containing the ring and mounted for measurement.

Figure 2. LIBS signals registered for the copper and lithium (internal standard) in different regions of the filter paper with a ring resulted from pre-concentrating 60 μL of a surrogate cachaça containing 5.0 mg L⁻¹ and 2.0 mg L⁻¹ of Cu and Li respectively.

Figure 3. Analytical curves obtained by (a) using the absolute intensity of the Cu emission line at 324.7 nm and (b) the ratio of emission intensities of the Cu and Li (at 670.80 nm).

Figure 4. Analytical curves showing the effect of the pre-concentrated volume on the LIBS detectability.

Figure 5. Emission spectra (of triplicate rings) showing the signal obtained for Pb (405.7 nm) present in a surrogate cachaça sample at 0.2 mg L⁻¹, compared with the signal of the blank. Pre-concentrated volume = 1500 μL.

Table 1 Results obtained for the evaluation of the repeatability of the ring-oven/mechanized LIBS proposed method for determination of Cu in cachaça.

Sample	**Replicate (mg L^{-1} of Cu)**			**Average (mg L^{-1})**	**Estimated Standard Deviation (mg L^{-1})**	**RSD* (%)**
	1	**2**	**3**			
			FAAS			
1	1.96	1.75	1.95	1.9	0.1	5
2	4.31	4.47	4.57	4.5	0.1	2
3	3.25	3.12	3.15	3.20	0.07	2
			Ring-Oven/Mechanized LIBS			
1	2.29	2.00	2.02	2.1	0.2	9
2	4.78	4.80	4.48	4.7	0.2	4
3	3.00	3.11	3.30	3.1	0.2	6

*Estimate of the relative standard deviation for triplicate measurement.

Table 2 Comparative results of the accuracy for the ring-oven/LIBS and the reference flame atomic absorption method.

Sample	FAAS (mg L^{-1})*	Ring-Oven/LIBS (mg L^{-1})*	Difference (mg L^{-1})
1	1.7 (0.1)	1.3 (0.3)	-0,.4
2	5.2 (0.2)	4.8 (0.4)	-0.4
3	3.3 (0.3)	3.4 (0.2)	0,1
4	3.4 (0.3)	4.9 (1.9)	1,5
5	0.5 (0.05)	0.5 (0.5)	0.0
6	2.0 (0.2)	1.0 (0.2)	-1.0
7	2.1 (0.05)	2.5 (0.4)	0.4
8	4.5 (0.2)	4.5 (11)	0.0

* Estimates of the relative standard deviation for triplicate measurement are shown between parentheses.

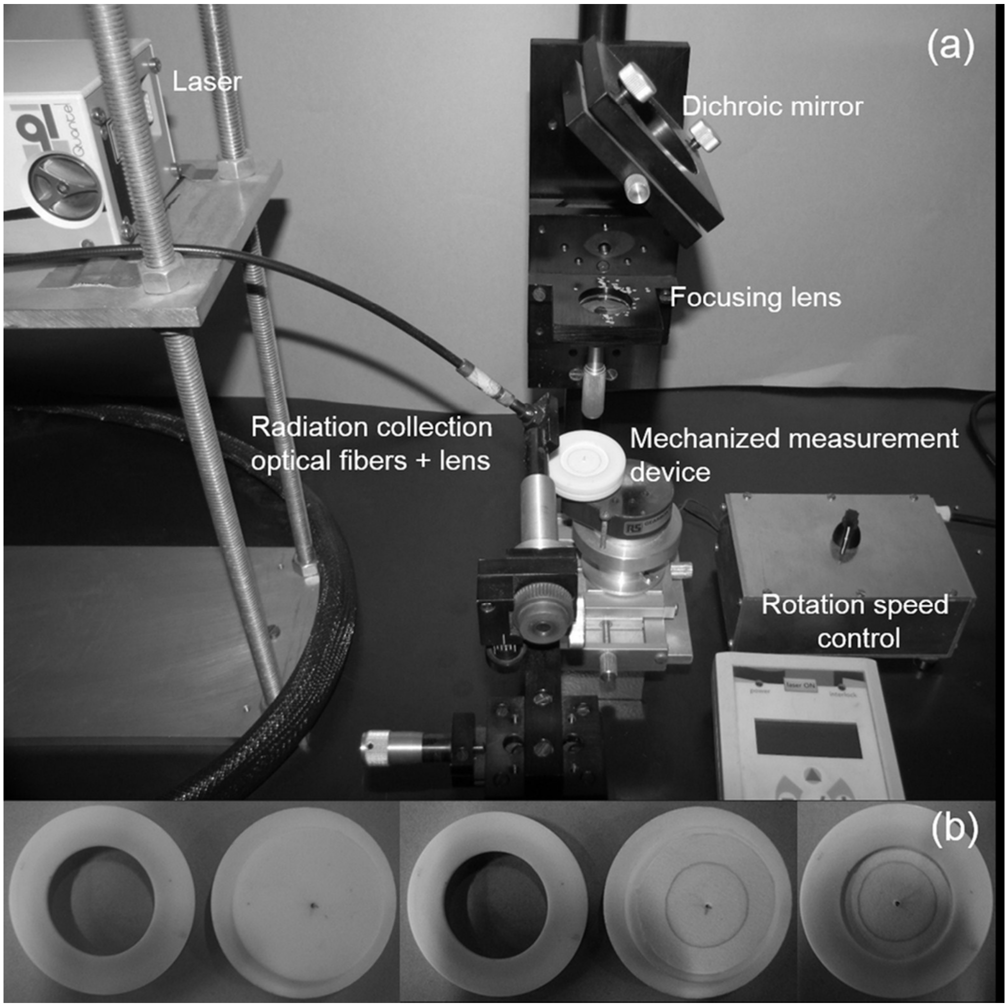

Figure 1. (a) Laser induced breakdown spectroscopic system and the mechanized device developed for ring oven measurement. (b) Detail of the spinning platform and cap with the filter paper containing the ring and mounted for measurement.

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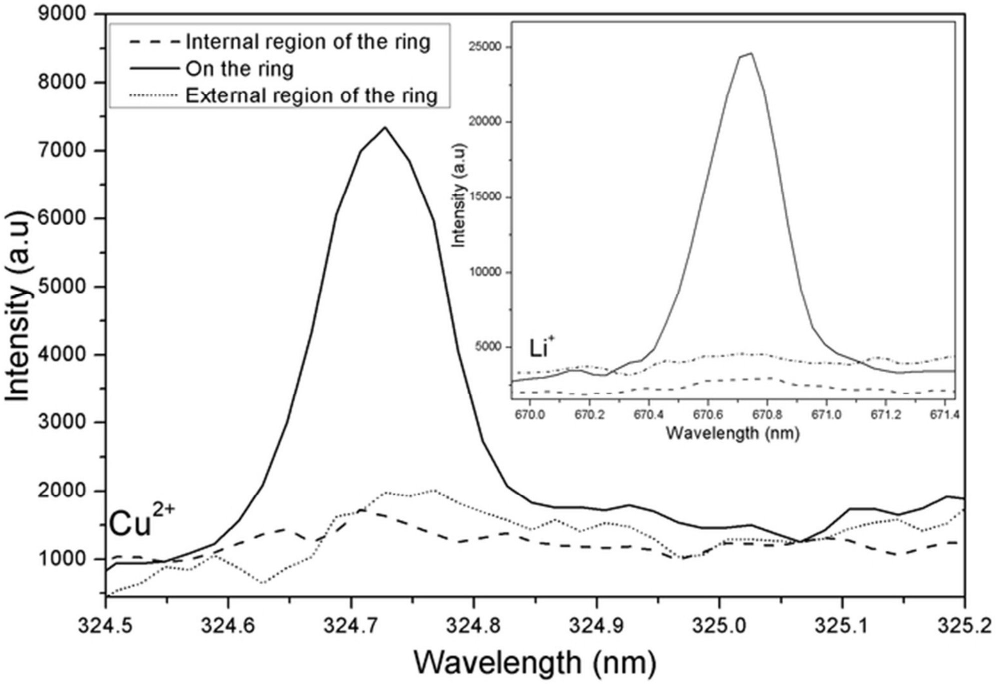

Figure 2. LIBS signals registered for the copper and lithium (internal standard) in different regions of the filter paper with a ring resulted from pre-concentrating 60 µL of a surrogate cachaça containing 5.0 mg L^{-1} and 2.0 mg L^{-1} of Cu and Li respectively.

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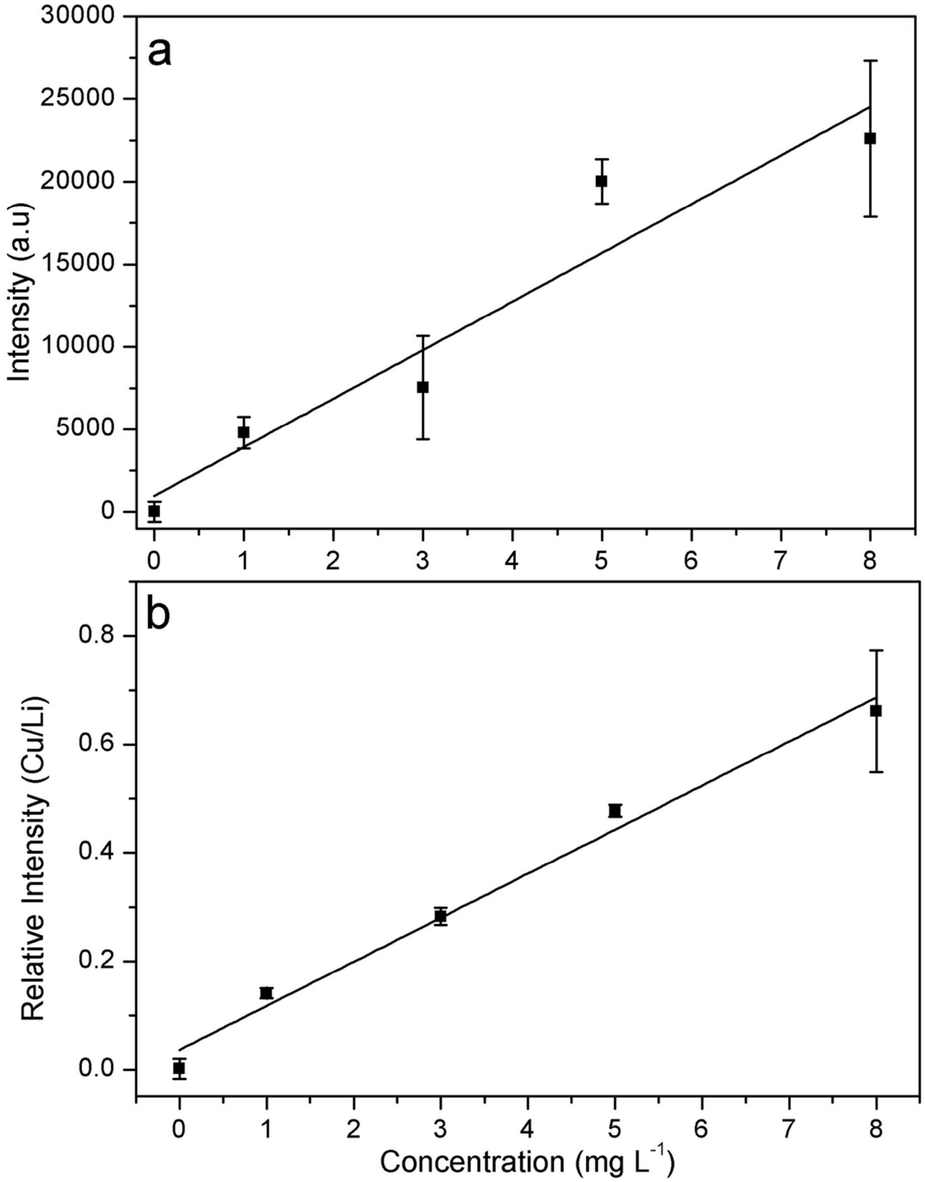


Figure 3. Analytical curves obtained by (a) using the absolute intensity of the Cu emission line at 324.7 nm and (b) the ratio of emission intensities of the Cu and Li (at 670.80 nm).

106x135mm (300 x 300 DPI)

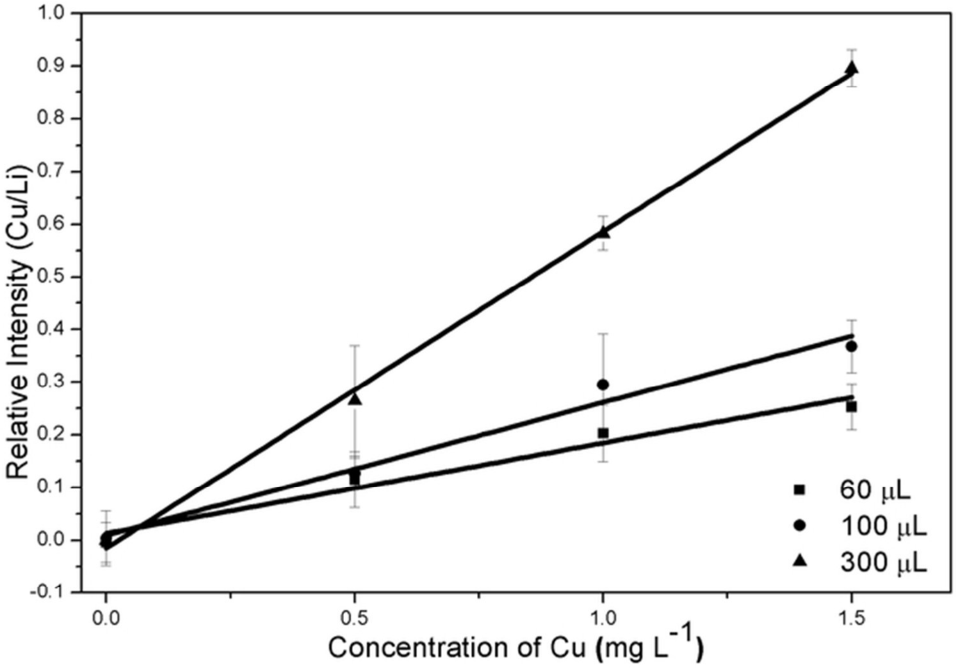


Figure 4. Analytical curves showing the effect of the pre-concentrated volume on the LIBS detectability.

58x40mm (300 x 300 DPI)

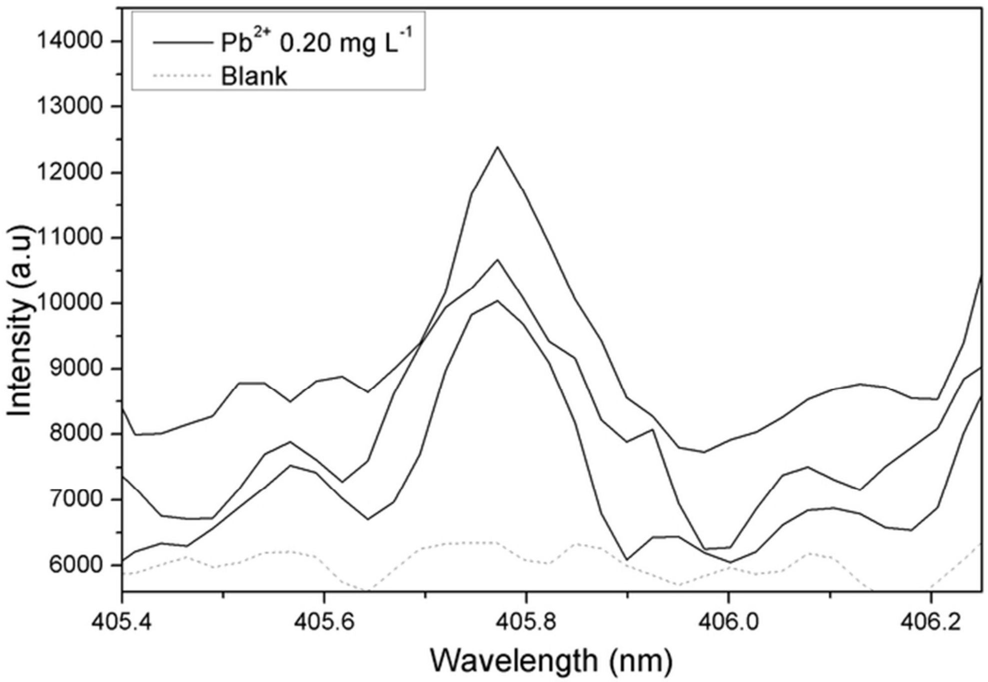
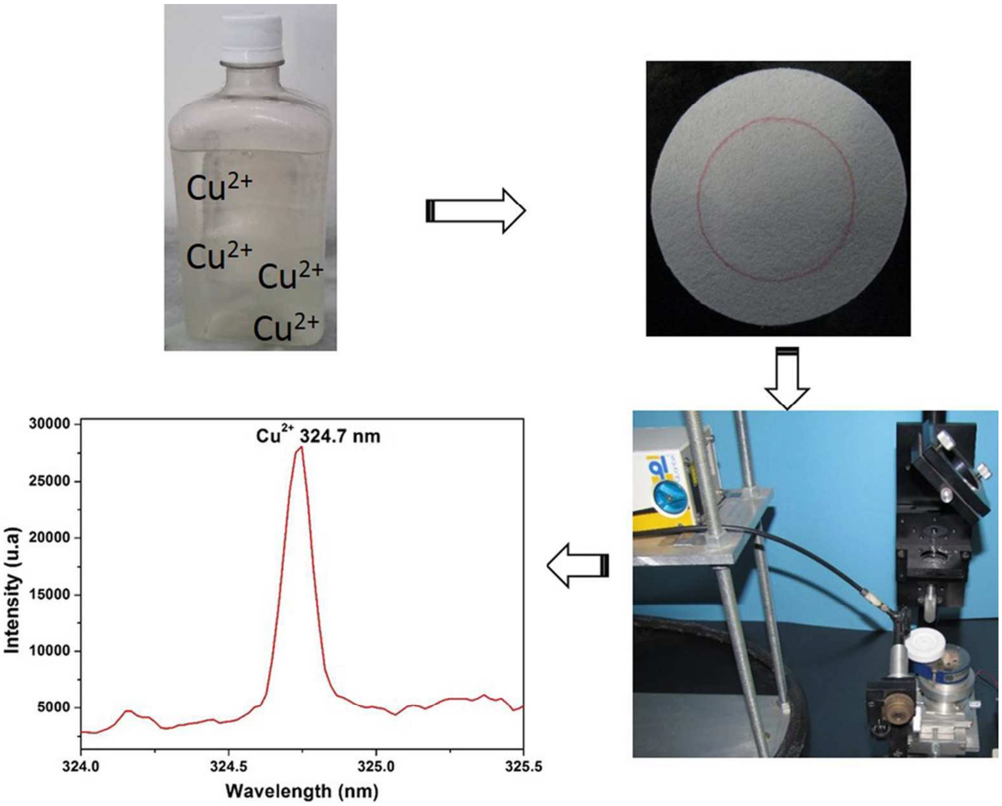


Figure 5. Emission spectra (of triplicate rings) showing the signal obtained for Pb (405.7 nm) present in a surrogate cachaça sample at 0.2 mg L^{-1}, compared with the signal of the blank. Pre-concentrated volume = 1500 μL.

58x40mm (300 x 300 DPI)



The mechanization of LIBS/Ring-Oven measurement and and a method for determination of copper in sugar cane spirit is presented

48x38mm (600 x 600 DPI)