An assessment of the applicability of the use of a plasticised PVC membrane containing pyrochatecol violet complexing reagent for the determination of Cu^{2+} ions in aqueous solutions by LIBS

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ABSTRACT

A plasticised PVC membrane containing pyrochatecol violet as complexing reagent has been used to extract and pre-concentrate Cu^{2+} ions from aqueous solution, aiming at their determination by Laser Induced Breakdown Spectroscopy. The membrane was prepared from a THF cocktail solution on a cellulose acetate support by the dip-coating technique, providing a homogeneous distribution of the complexing reagent and a thickness of 3 μm. The extraction was straightforwardly performed by immersing the membrane in the Cu^{2+} sample solution buffered at pH 6.0 with sodium acetate. The extraction time defined the working analytical range (from μg L^{-1} to mg L^{-1}) and a 50-min extraction provided a detection limit of 15 μg L^{-1} for Cu^{2+} ions. The membrane is stable for at least 2 months when stored in a desiccator, allowing in-field extractions, that avoid sampling, storage and transport of the aqueous sample to the laboratory.

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1. Introduction

Techniques based on atomic spectroscopy usually require a sample preparation step, which is, as a rule, time consuming, besides increasing the cost of the analysis and the generating of residue. Among these techniques, Laser Induced Breakdown Spectroscopy (LIBS) [1,2] can be highlighted because it is fast, multielemental, requires no or little sample preparation, allowing real time and in-situ analysis of gaseous, liquid and solid samples [3].

LIBS measurements consist of focalising a laser pulse onto a small area of the sample surface, which will vaporise a given amount of the material surrounding the point of incidence, producing a high temperature plasma that triggers the processes of atomisation and excitation, followed by emission of light by the excited species, such as atoms, ions and molecules [3]. Despite its simplicity and versatility, direct LIBS measurements of liquids show high limits of detection, which are inappropriate for many analytical applications. Dissolved gases and particulate matter can impair the focus of the laser beam and solvent splashing can noticeably affect the stability of the plasma, causing, as a consequence, a decrease in the detectivity and the repeatability of the measurements due to the suppression of emission. In addition, part of the laser energy is employed to vaporise water, also contributing negatively to signal intensity and repeatability. In order to avoid splashing,

water samples have been frozen in liquid nitrogen before measurements [4,5], because ice provides a flat surface, preserving the homogeneity of the water sample. However, the limits of detection achieved by this strategy are still high, falling in the mg L^{-1} range.

The transfer of the analyte from a liquid sample to a solid substrate seems to be an elegant strategy to overcome the above-mentioned drawbacks, as the surface of a solid can be well-defined and regular, facilitating focusing the laser and the position of the breakdown. Additionally, the transfer of the analyte can be accompanied by its concentration in the solid substrate, which contributes to the improvement of detection limits. Several substrates have been used as sorbent, such as graphite [6,7], ion exchange membranes [8], paper [9,10], calcium hydroxide [11], wood [12], aluminium [13–15] and bamboo charcoal [16]. Different schemes have been employed for transfer of the analyte to these solid substrates, imparting lower limits of detection. For example, a drop of sample solution has been deposited on the surface of a graphite sheet and heated to dryness for LIBS measurements, achieving limits of detection of 10 μg L^{-1} for several metal ions [6] and for boron [7]. Engine oil has also been transferred dropwise to filter paper for determination of several metal ions, providing limits of detection from 2 to 29 mg L^{-1} for single-pulse LIBS analyses [9]. Filter paper has also been proposed for concentration of sodium, iron and copper based on the ring-oven technique, achieving limits of detection of 700, 400 and 300 μg L^{-1}, respectively [10]. Concentration has been accomplished by filtering the sample solution through an ion exchange membrane, imparting detection limits as low as 4 μg L^{-1} for copper [8]. Calcium oxide has been

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added to the sample solution in order to transfer the analyte to a solid matrix by precipitation of calcium hydroxide, reaching detection limits of 1.2 mg L^{-1} [11]. Bamboo charcoal has been also added to the sample solution as a solid-phase extraction adsorbent, being filtered and dried at 105 °C before the preparation of KBr pellets. A detection limit of 8.5 mg L^{-1} has been achieved for lead [16]. Wood slices have been immersed in a sample solution aimed at extracting metal ions, providing detection limits of 29 μg L^{-1} for copper when an immersion time of 2 min is employed [12]. Electrical deposition on aluminium surfaces has been used to extract metal ions from aqueous samples and limits of detection of 83 μg L^{-1} [13], 0.2 μg L^{-1} [14] and 16 μg L^{-1} [15] have been reached for copper.

High molar mass poly(vinylchloride) (PVC) has been extensively used for the preparation of ion-selective membranes for the development of optical and electrochemical sensors, due to its mechanical properties, transparency, homogeneity and easy membrane preparation. Additionally, there are several different plasticisers which are used in the formulation of the membrane with the purpose of lowering the glass transition temperature below ambient temperature, improving the mobility of the (chromo)ionophore and metal ion [17]. The versatility of the PVC membranes allows the development of sensors for a vast variety of metal ions and, in the case of optical sensors, the membranes can offer a reversible or irreversible response [18]. The transfer of the metal ion to the PVC membrane is usually accompanied by concentration of the analyte, as the pH of the solution is adjusted in order to favour the reaction between the metal ion and the (chromo)ionophore. Therefore, the use of a PVC sensing phase as an extracting membrane can be an alternative for transferring the metal ion from the aqueous solution to the solid phase, improving the limits of detection of LIBS.

In the present work, with the purpose of demonstrating the viability of using this strategy in LIBS analysis, a plasticised PVC membrane containing pyrocatechol violet as complexing reagent [19] was chosen to extract Cu^{2+} ions from aqueous solutions. The PVC membranes were prepared by dip-coating onto a cellulose acetate support and extractions were performed by immersion of the sheet into a Cu^{2+} ion solution. The extraction time was investigated as a function of the concentration of the Cu^{2+} in the solution, demonstrating that the limits of detection can be improved by choosing appropriate extraction time.

2. Experimental

2.1. Reagents and solutions

High molar mass PVC (Fluka), bis(2-ethylhexyl)sebacate (DOS, Sigma), cetyltrimethylammonium bromide (CTAB, Sigma), copper nitrate pentahydrate (Merck), sodium acetate (Synth), pyrochatecol violet (PV, Merck), hydrochloric acid (Merck) and sodium hydroxide (Merck) were used as purchased. Tetrahydrofuran (THF, Synth) was distilled before use.

Cu^{2+} reference solutions in the range from 20 μg L^{-1} to 200 mg L^{-1} were prepared in pH 6.0 sodium acetate buffer from a 1000 mg L^{-1} Cu^{2+} stock standard solution.

2.2. Preparation of the PVC membrane

Plasticised PVC membranes were prepared based on the procedure described by Steinberg et al. [19]. A mixture containing 40.0 mg (31.3 wt.%) of PVC, 79.6 mg (62.4 wt.%) of DOS, 4.0 mg (3.1 wt.%) of PV and 4.0 mg (3.1 wt.%) of CTAB was dissolved in 1.5 mL of distilled THF and placed in an ultrasonic bath for 30 min for homogenisation. A 1.0×2.5 cm cellulose acetate strip was immersed in this solution and removed at a constant velocity (10 cm min^{-1}), forming homogeneous membranes on both sides of the support with thicknesses of 3.0 μm after the evaporation of the solvent. The extracting membranes were kept in a dessicator before use, presenting lifetimes of at least 2 months.

2.3. Extraction of the Cu^{2+} ions

The extraction of the Cu^{2+} ions from the aqueous sample was performed by immersing the membrane into 20 mL of solution, whose pH was adjusted to 6.0 with acetate buffer. Extraction times varied from 20 to 50 min, depending on the Cu^{2+} concentration in the solution. After extraction, the excess of water on the membrane was removed with a soft tissue paper before acquiring the spectrum by LIBS.

2.4. Apparatus and data acquisition

The LIBS system consisted of a Nd:YAG (Quantel, Brio) pulsed laser, running at 1064 nm (fundamental wavelength), an echelle polychromator with resolution of 0.04 nm at 250 nm (Mechelle 5000, Andor Technology) and an ICCD camera (1024 × 1024 pixels, iStar DH 734, Andor Technology) [10]. The echelle polychromator was calibrated as recommended by the manufacturer, employing a mercury/argon light source. A 5 ns laser pulse (energy of 110 mJ pulse^{-1}; irradiance of 7.0×10^{11} W cm^{-1} and focal spot of 60 μm) was employed to generate the microplasma; the emitted radiation was collected by an optical fibre (50 μm diameter), directed to the polychromator, before reaching the camera for spectrum acquisition in the 200–850 nm range. A delay time of 1 μs and an integration time of 1 μs were employed in all measurements.

Duplicate measurements were performed by probing both sides of the strip. For each side, 10 spectra were acquired at different locations of the extracting membrane and accumulated by the equipment, resulting in a single emission spectrum.

3. Results and discussion

Pyrocatechol violet is a water-soluble, non-selective complexing reagent used for the spectrophotometric determination of several metal ions, such as Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Bi^{3+}, In^{3+} and Al^{3+} [20]. It has been immobilised on solid supports for pre-concentration and determination of metal ions by atomic absorption spectrometry. Chromosorb 105 was used as the solid support in the determination of Cu^{2+} [21], while XAD-2 resin was used in the determination of Zn^{2+}, Cd^{2+}, Ni^{2+} and Pb^{2+} [22]; and Pb^{2+} and In^{3+} [23]. The selectivity of a complexing reagent can change after immobilisation due to its interaction with the solid matrix, which can affect, for example, the acidic constant values and the ability of forming complexes of high stoichiometry. When immobilised as a lipophilic ion-pair with tetraoctylammonium anion in a plasticised PVC membrane, the selectivity of PV for Cu^{2+} ions is enhanced because the immobilisation of the reagent favours the formation of 1:1 complex, which is the case for Cu^{2+} ions [19].

The homogeneity of the extracting membrane is fundamental to guarantee the repeatability of the LIBS measurements. Initially, the membrane was prepared by manual deposition of a 10-μL drop of the cocktail solution on the cellulose acetate support. After evaporation of the THF solution, a spot with diameter of ca 5 mm was obtained, presenting a semi-spherical shape and an inhomogeneous distribution of the complexing reagent. In addition, its small area made it hard to obtain a series of spectra with the same membrane. On the other hand, membranes prepared by dip-coating offered appropriate homogeneity and larger areas, as well as two workable sides that extended its analytical capability. Thus, each side of the strip was used to produce an averaged spectrum (10 laser shots), allowing duplicate measurements from a single extraction.

Preliminary experiments were performed in order to identify the appropriate emission lines for determination of Cu^{2+}, considering that the extracting membrane could also produce emission lines that would overlap with those of the analyte. To this end, one membrane was immersed in a pH 6.0 acetate buffer solution and another

was immersed in a 200 mg L^{-1} Cu^{2+} solution also buffered at pH 6.0 for a period of 20 min. A highly concentrated solution was used in order to guarantee a high intensity signal, facilitating the identification of the emission lines. A pH 6.0 was employed as recommended by Steinberg et al. [19], based on the mechanism of exchange of proton by Cu^{2+} in the PVC membrane, as well as the apparent pK of the complexing reagent in the PVC membrane. Additionally, Buke et al. [21] have demonstrated that the PV-Cu^{2+} complex is entirely adsorbed on Chromosorb 105 resin above pH 5.0, result that corroborates that the process is highly driven towards the formation of the complex in the experimental conditions employed in the present work. Fig. 1 shows the spectrum region from 324 to 328 nm, where there are emission lines for the Cu neutral atom (Cu (I)) and the membrane presents no interfering signal. The atomic emission lines at 324.75 and 327.39 nm were chosen according to the NIST database [24]; the difference between the emission maxima of the experimental measurement and the NIST database is within the resolution of the echelle polychromator. The emission intensity at 324.75 nm was employed in all measurements throughout the present work.

The enrichment capability of the membrane was evaluated by performing extractions at different time intervals (from 5 to 60 min) with a buffered 40 mg L^{-1} Cu^{2+} solution. As can be seen in Fig. 2, the signal intensity is enhanced as the extraction time increases, converging to membrane saturation after 60 min of extraction. This result indicates that the working concentration range can be tailored by adjusting the extraction time. Naturally, for more dilute solutions (in the µg L^{-1} concentration range) extraction times longer than 60 min can be used without saturation of the membrane.

Fig. 3 shows the analytical curves obtained for Cu (I) species, after extracting the ion for 20 min from aqueous solutions with concentrations ranging from 0.10 to 0.80 mg L^{-1} and 10 to 100 mg L^{-1}. These results demonstrate the versatility of the proposed strategy of transferring metal ions from the aqueous solution to the solid matrix, as the analyte can be determined at different concentration levels. The performance of this procedure can be even improved if longer extraction times are employed. For example, Fig. 4a shows the spectra provided by the extracting membrane after extraction times of 20 min and 3 days for a 100 µg L^{-1} Cu^{2+} ion solution, unequivocally indicating that the detectability can be improved. In addition, for Cu^{2+} ion solutions in the concentration range from 20 to 100 µg L^{-1}, whose spectra are shown in Fig. 4b, a linear response (signal intensity $=765$ (± 23) $+ 4.21$ (± 0.36) * [Cu], $r^2 = 0.985$) is obtained for extraction time of 50 min, achieving a detection limit of 15 µg L^{-1}, calculated according to Miller and Miller [25]. The LOD obtained in the present work is comparable to those described in the literature [6–8,12,13,15], demonstrating the potential of the proposed liquid-to-solid transfer procedure for determination of metal ions in water at low concentrations. Although electrical deposition can
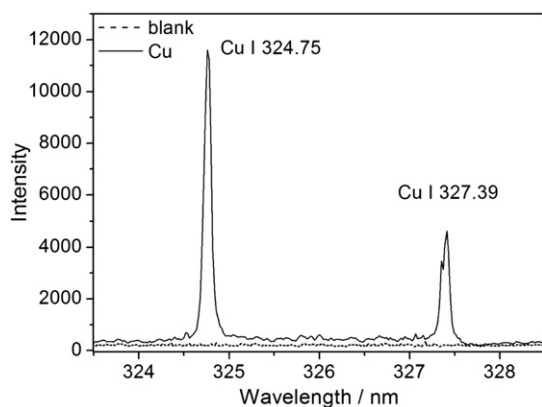
achieve detection limit as low as 0.2 µg L^{-1} [14], it must be emphasised that the procedure described in the present work does not require the assistance of any equipment to perform the extraction, which constitutes a great advantage, as in-field extraction can be straightforwardly performed.

The use of PVC extracting membranes seems to be a powerful tool for transferring metal ions from liquid samples to a solid matrix. It is important to stress that there is an extensive variety of complexing reagents, whose chelating properties allow preparation of membranes that can be selective for a group of metal ions or even specific for a given species. If a selective complexing reagent is used, the multi-elemental capability of LIBS can be fully explored. In this case, the competition for the complexing sites of the reagent by each

Fig. 2. Emission signals obtained with a 40 mg L^{-1} Cu^{2+} solution as a function of the extraction time (324.75 nm spectral line of Cu neutral atom).

Fig. 3. Analytical curves for Cu after 20 min extraction from Cu^{2+} in the concentration ranges of 0.10 to 0.80 mg L^{-1} (A) and 10 to 100 mg L^{-1} (B) (intensity at 324.75 nm spectral line of Cu neutral atom).

Fig. 1. Emission lines for Cu neutral atom, after extraction for 20 min by the PVC membrane from a 200 mg L^{-1} solution buffered at pH 6.0.
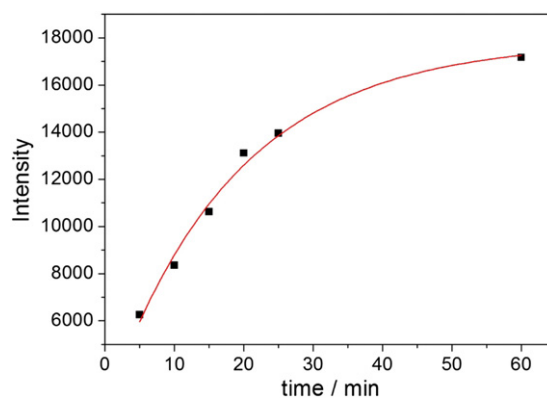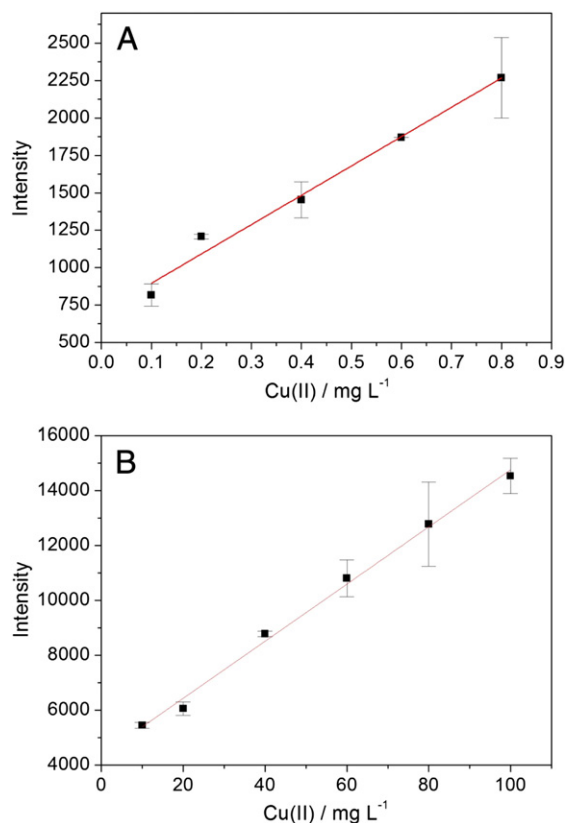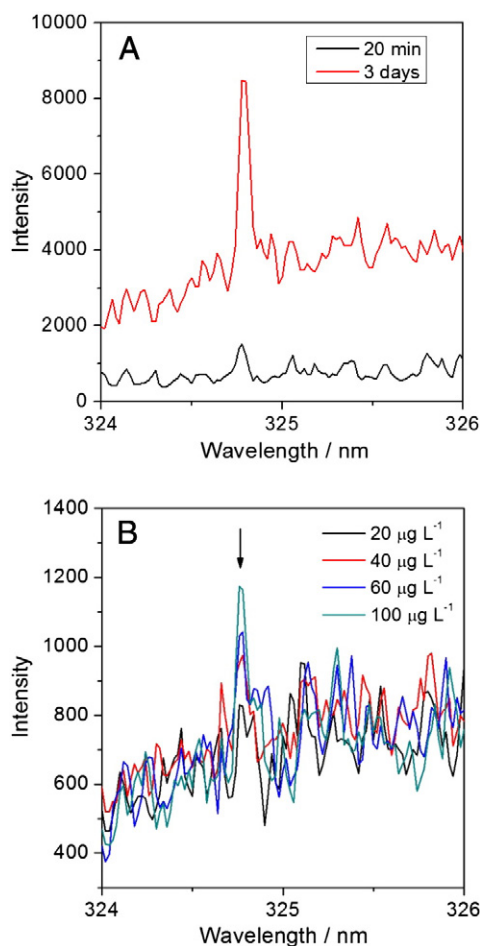
Fig. 4. Spectra of Cu neutral atom after extraction times of 20 min and 3 days from a 100 μg L^{-1} Cu^{2+} ion solution (A) and after extraction time of 50 min from 20 to 100 μg L-1 Cu^{2+} ion solution (B). The arrow indicates the Cu neutral atom signals.

analyte is taken into account by means of an analytical curve constructed with the use of multi-elemental standard solutions. However, if spectral interferences are severe, experimental conditions, such as pH of the sample solution and use of chelating reagents, can improve the specificity of the extraction, avoiding these spectral interferences in LIBS determination, as it has been done in liquid–liquid extraction procedures for metal ion concentration for atomic spectrometry. In addition, the PVC membrane prepared by dip-coating presents a flat surface, with a homogeneous distribution of the complexing reagent, which facilitates the LIBS measurements, improving repeatability.

4. Conclusions

The use of plasticised PVC extracting membrane to transfer metal ions from aqueous solutions to a solid matrix, with concomitant concentration of the analyte, has been demonstrated as a potential tool for improving the detection limits of LIBS. By immobilising pyrochatecol violet in a PVC membrane plasticised with bis(2-ethylhexyl)sebacate it was possible to achieve a detection limit of 15 μg L^{-1} for Cu^{2+}, by employing an extraction time of 50 min. The useful analytical range can be tuned by adjusting the extraction time. The membrane is easy to prepare, stable for at least 2 months, allowing in-field extractions and avoiding the sampling, storage and transport of the sample to the laboratory, which are critical steps in the analytical process that can impair the accuracy and precision of any method. Finally, it must be remembered that in the case of a specific application, which means the target analyte(s) and

the sample matrix, a plasticised PVC membrane containing a suitable complexing reagent must be developed. Additionally, the extraction protocol (pH of the solution, buffer composition, extraction time, use of chelating reagent to avoid chemical interference) also needs to be optimised, in order to achieve the best performance of the method.

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