Received: 19 August 2021 | Revised: 16 September 2021 | Accepted: 17 September 2021

DOI: 10.1002/jssc.202100660

JOURNAL OF SEPARATION SCIENCE

REVIEW ARTICLE

Wooden-based materials: Eco-friendly materials for direct mass spectrometric analysis and microextraction

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Funding information
Spanish Ministry of Science, Innovation, and Universities, Grant/Award Number: FPU19/01488; Ministerio de Ciencia e Innovación, Grant/Award Number: PID2020-112862RB-I00; Funding for open access charge, Grant/Award Number: Universidad de Córdoba / CBUA

Lignocellulosic materials have arisen as a sustainable alternative in microextraction techniques during the last 10 years. As they are natural materials, their use fits into some of the principles of Green Analytical Chemistry. Their inherent porosity, narrow shape, and rigidity permit their use in ambient ionization mass spectrometry techniques. In particular, the combination of wooden-based materials and direct analysis gives birth to the so-called wooden-tip electrospray ionization mass spectrometry technique. This approach has been used for the direct analysis of complex samples, and as a streamlined tool for fingerprint quality analysis. Also, wooden-based materials can be superficially modified to boost the interaction with target compounds, allowing their isolation from complex samples. This review describes the potential and applicability of direct analysis using lignocellulosic materials, as well as other alternatives related to their use in microextraction.

KEYWORDS
lignocellulosic materials, mass spectrometry, microextraction, sustainability, wood

1 | SAMPLE PREPARATION FROM A GREEN PERSPECTIVE: THE ROLE OF LIGNOCELLULOSIC MATERIALS

In the last decades, analytical chemists have become aware of the potential environmental impact of their activities. The definition of Green Analytical Chemistry (GAC) principles can be considered a milestone in this evolution [1,2]. The first GAC principle suggests the direct analysis of the samples, avoiding any treatment. In other words, sample preparation is identified as a step, or combination of steps, with a potential environmental impact due to the energy and resources (reagents, solvents) required. Although ambient ionization mass spectrometry (AIMS) techniques have opened the door to rapid determinations, in most cases, direct analysis is somewhat challenging due to the complexity of the sample matrices and the low concentration of the target compounds, which usually fall below the limit of detection of the instrumental techniques. Also, guidelines (for example, pollutants

Article Related Abbreviations: AIMS, ambient ionization mass spectrometry; DI, direct infusion; FI-WT-ESI-MS, field-induced wooden-tip electrospray ionization mass spectrometry; GAC, green analytical chemistry; MC, metallic capillary; MIPCWT, molecularly imprinted polymer-coated wooden toothpick; SSMS, substrate-spray mass spectrometry; WAC, white analytical chemistry; WC, wooden capillary; WT-ESI-MS, wooden-tip electrospray ionization mass spectrometry; WT, wooden toothpick

concentration thresholds) become increasingly stringent over time, and they can only be fulfilled by a rational combination of sample preparation workflows and high-performance instrumental techniques. White analytical chemistry (WAC), a recently coined concept, tries to integrate this new vision [3]. WAC aims to align the green perspective with the first objective of our discipline, that is, obtaining useful chemical information about the systems under study. Once this first objective is guaranteed, the green aspects come into play. Sample preparation has evolved in the last decades following three main driving forces: simplification, miniaturization, and automation [4]. Apart from the positive effects on the analytical performance, these trends allow to reduce the environmental impact by minimizing the reagents, solvents, and energy needed.

The 10th principle of GAC proposes a new way to make our developments more environmentally friendly using removable materials as resources. The synthesis of new solvents and sorbents based on natural products or generated by the valorization of biomass or wastes can be considered as a current trend in sample preparation. Natural deep eutectic solvents [5,6] and bio supramolecular solvents [7] are examples of solvents obtained from natural precursors and having a low environmental impact. Lignocellulosic materials (involving cellulose, cork, and wood) have been proposed for the synthesis of functional sorbents in microextraction techniques [8,9].

Cellulose is the most abundant biopolymer on earth, and it has been used, commonly as paper or cotton, for designing new sorbents in microextraction. Paper consists of the irregular packing of cellulose fibers providing a flat material with high porosity and surface area. Although it can be used without further modification [10,11], its modification with sorptive phases [12] is usually preferred to improve the capacity or changing the extraction selectivity. Paper can be modified by the physical deposition of polymers on its pores [13,14], by the immobilization [15–18] of extracting groups in its surface, or by its partial carbonization [19]. The flat shape and porosity of paper have permitted its easy combination with instrumental techniques simplifying the overall analytical procedure [20]. Cotton, consisting of low-packed cellulose fibers, has been also used in recent years for the synthesis of novel sorbents. It can be easily modified following similar approaches to those used for paper. For example, cotton-polymer composites can be synthesized by the physical deposition of polymers using the dip-coating technique [21]. Also, cotton fibers can be modified, including special groups in the surface, to tune the extraction selectivity [22–25]. The controlled pyrolysis of cotton provides carbon fibers [26,27], whose polarity can be adapted to the target analytes by the proper selection of the synthetic conditions [28].

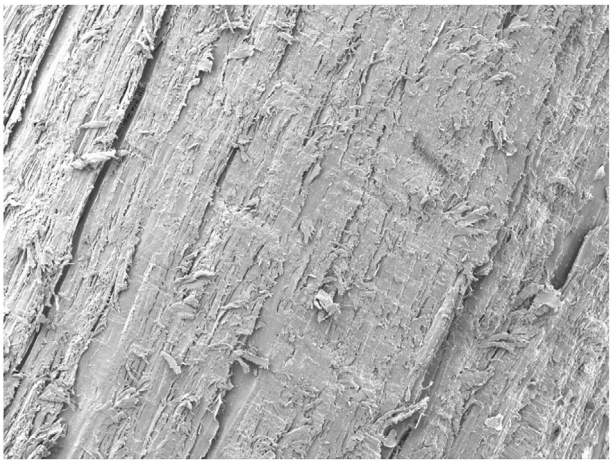

FIGURE 1 Scanning electron microscopy image of the surface of a wooden toothpick at 100x magnifications. Reproduced with permission of Elsevier from reference [52]

Cork is the bark of the cork oak tree and combines hydrophobic (suberin and lignin) and hydrophilic (cellulose and hemicellulose) polymers in its structure, thus providing a lipophilic and hydrophilic balance [29]. The versatility of cork has been demonstrated by its use as a sorptive phase in different microextraction techniques, including SPME [29], bar adsorptive microextraction [30], and rotating disk microextraction [31,32].

Wooden materials are composed of a natural polymeric structure of cellulose, hemicellulose, and lignin, as well as minor components such as volatile organic compounds. The cellulosic composition implies the presence of superficial hydroxyl groups, providing a hydrophilic character to this material and permitting their modification by covalent reactions (e.g., silanization). The hydrophobic nature of lignin improves the hydrophilic/lipophilic balance of wood, opening the door to the isolation of organic compounds with different polarities. Wood is highly porous due to the presence of microchannels, although different procedures like surface polishing can reduce the porosity of the materials, as is observed in Figure 1. Wood is a worldwide available product that is cheap, biodegradable, and stable. This affordability allows designing disposable extraction units, thus avoiding cross-contamination and memory effects.

2 | WOODEN-TIP ESI-MS FOR DIRECT ANALYSIS OF SAMPLES

2.1 | Principles of direct MS

AIMS techniques permit the direct analysis of samples with minimal or no sample preparation. Within the

existing alternatives, substrate-spray mass spectrometry (SSMS) techniques [33] are especially relevant as they allow the direct combination of microextraction techniques with MS, avoiding the usual chromatographic separation of the analytes [34]. This simplification of the analytical procedure, removing the chromatographic separation, provides a higher sample throughput at the expense of a selectivity loss that can be compensated by MS, mainly if high-resolution MS is applied.

SSMS consists of applying a high electrical potential over a substrate where the sample or elution media has been located. The potential induces the electromigration of the liquid phase through the materials to the substrate tip where an electrospray is formed, and the ionized analytes are finally focused on the MS inlet [35]. The substrate can be used as an inert material where the sample is just deposited and analyzed. However, the substrate may play a more active role. In the latter approach, the substrate can be used as a microextraction device to isolate the analyte from the sample matrix and finally assist their determination by substrate-spray MS.

2.2 | Wooden tips as substrates in direct MS, a general characteristic of wooden-tip ESI-MS

The shape and porosity of the substrate are critical for SSMS performance. Wooden toothpicks (WTs), by far the most used wooden material format, present a sharped geometry, hardness, and narrow shape that can be exploited in SSMS. The narrow shape of WTs avoids the rapid transversal diffusion and vaporization of solvents, providing a longer stable spray than metal tips and paper substrates. This aspect has an evident impact on the sensitivity levels [35]. WTs also have a sharpened tip that provides an efficient Taylor cone. The potential of WTs as substrates is so powerful that it has given birth to a particular technique named wooden-tip ESI-MS (WT-ESI-MS). The schematic procedure of the technique is depicted in Figure 2.

The first reported use of WTs in SSMS is attributed to Hu et al. in 2011. This novel procedure permitted the qualitative analysis of different types of analytes, including organic molecules, organometallic compounds, peptides, and proteins. Also, the WT-ESI-MS analysis was not only limited to liquid samples but also permitted the analysis of slurry and powder samples. This first contribution article settled the bases regarding the potential application of WT-ESI-MS in forensic analysis, the identification of proteins in metabolomics, and the analysis of complex samples. The authors demonstrated the linear relationship between the volume of eluent (in the μL range) with the

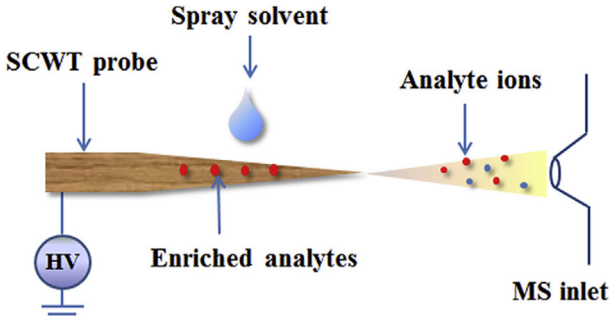

FIGURE 2 Schematic representation of the wooden-tip ESI-MS (WT-ESI-MS) procedure. SCWT, surface coated wooden tip. Reproduced with permission from Elsevier [38]

duration of the signal. This analytical response, in terms of sensitivity, was similar to the obtained in paper-spray MS, but the signal time was longer in the case of WTs according to their narrow and microchannel-based structure that tends to focus the spray to the MS inlet instead of spreading, which is the case of paper [36]. The performance of WT-ESI-MS can be affected by several parameters well reported in the literature. The applied capillary voltage varies between 2.5 and 6.0 kV. The length of WTs is usually around 2 cm since larger values restrict the efficient formation of the electrospray due to the electrical insulator nature of wood. The WTs outer diameter spans between 0.15 and 0.2 mm because sharper tips provide more intense signals than wider sizes. The distance between the WT and the MS inlet is usually fixed between 5 and 10 mm, although Yang and Deng reported that shorter distances than 10 mm might provoke electro-discharges [37]. The sample or eluent loading volume ranged between 1 and 10 μL. Concerning the eluent volume, the first time of desorption implies approximately 85% of the signal compared to further desorption steps [35,38]. According to Yang and Deng, the eluent volume affects the duration of the signal but not its intensity [37].

In summary, WT-ESI-MS implies a low solvent and sample consumption (in the μL order), allowing the direct detection and quantitation of analysis in complex samples. This technique reduces the analysis time as sample pretreatment is minimized (or eliminated) and avoids chromatographic separation [39,40]. WT-ESI-MS presents several advantages, including (i) easy setup and compatibility with diverse instruments [39], (ii) high throughput analysis of samples [41], (iii) prevention of clogging in the classic capillary ESI, (iv) avoids cross-contamination by using disposable WTs [42], and (v) presents a high enrichment capacity with an effective matrix removal [43]. Consequently, WT-ESI-MS has been used for different applications, including the identification and quantitation of analytes in complex samples (e.g., biofluids, plants), the

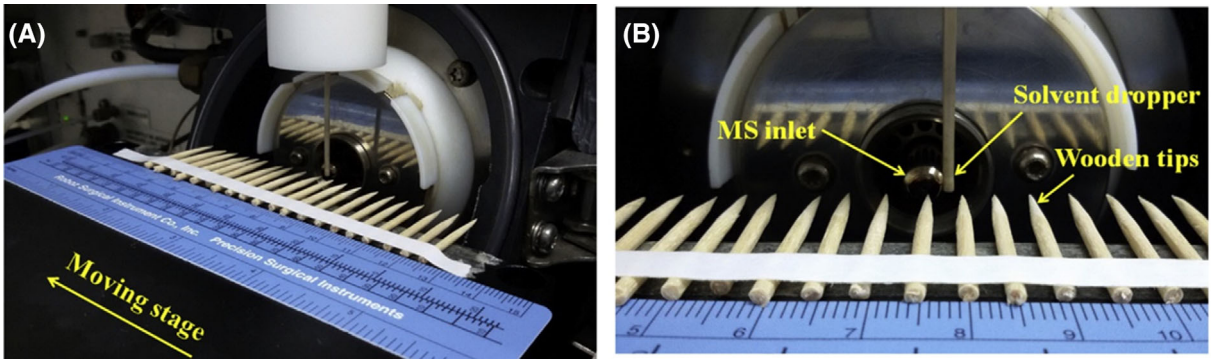

FIGURE 3 Configuration of the high sample throughput field-induced wooden-tip ESI-MS (FI-WT-ESI-MS) technique. (A) General view and (B) detail of the solvent dropper used to add the spray solvent into the wooden toothpicks (WTs). Reproduced with permission from Elsevier [46]

direct analysis of raw samples, living plants, peptide, protein, and metabolic analysis, and authenticity of raw plant-based samples, among others.

2.3 | Methodological innovations in WT-ESI-MS

In the last years, several groups have reported relevant innovations in the WT-ESI-MS technique that will open new perspectives in the field. Hu et al. have suggested the double role that modified WTs may play in WT-ESI-MS. They synthesized tips superficially modified with different functional groups (namely: C_{18}, NH_2, and SO_3H) that can interact with the target analytes by different interaction mechanisms. The authors evaluated the modified WTs under two different workflows. In the first workflow, the WTs are used as simple substrates for the direct MS analysis. The samples are deposited over the WTs and dried. After this step, an eluent is added to the WT under the application of a high voltage to produce the spray in the tip thus introducing the analytes in the MS. The detection of analytes that develop weak interactions with the WTs is favored in this workflow because they are easily sprayed out for detection, allowing to minimize the effect of those matrix components able to develop stronger interactions with the WT phase. In the second workflow, the WTs are used as both sorbents and MS substrates. The WTs are introduced in the sample to isolate and enrich the analytes. Once the extraction is performed, the WTs are finally analyzed by WT-ESI-MS. This strategy provides better signals for those analytes able to interact with the tip since this interaction permits their selective enrichment. This extraction-analysis strategy improves the selectivity since some matrix components are not retained in the tip or efficiently removed during the washing step [44]. This preliminary study demonstrates that the WTs can be used a pseudo chromatographic column to separate analytes before their final determination. Using a vegetable extract as sample, the same group has demonstrated that the analytes can be separated in the WTs based on their polarity. This strategy, that allowed the direct analysis of protein samples in the presence of a high salt medium, can be extrapolated to bioanalytical applications [45].

Although WT-ESI-MS analysis is rapid, the sample throughput is somewhat limited because the WTs should be manually replaced after every sample analysis. To avoid this limitation, Yang and collaborators reported a contactless high throughput procedure, named field-induced WT-ESI-MS (FI-WT-ESI-MS) (Figure 3). In contrast to the conventional approach, in this technique, the high voltage is applied to the MS inlet while the tip is maintained at 0 V. The pre-loaded WTs are immobilized on a moving stage connected to a peek tube (noted as a solvent dropper in Figure 3) attached to a syringe pump with a 5 mL syringe that supplies the spray solvent at a constant flow rate of 0.2 mL/min. This outstanding procedure provides an analysis time of 6 s/sample in both positive and negative mode. FI-WT-ESI-MS was used for the quality assessment of herbal medicines in terms of origin and authenticity [46]. Hu et al. also developed a high throughput WT-ESI-MS procedure, similar to the previously commented, but applying the high voltage directly to the WTs. This methodology permitted the detection of adulterated drugs in herbal dietary supplements [47].

Other studies are related to the use of WT-ESI-MS toward the direct detection of proteins in raw biological samples. Hu et al., reported the mechanism of solid-substrate ESI-MS using non-polar solvents allowing the determination of native proteins [48]. Another approach is related to the description of the reactive-WT-ESI-MS procedure, in which a reagent is added onto a preloaded WT and protein-ligand complexes are generated and subsequently detected. This alternative allowed the

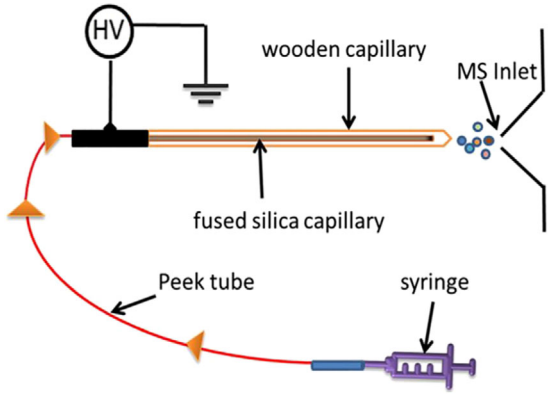

FIGURE 4 Configuration of the wooden capillary (WC)-ESI-MS procedure. Reproduced with permission from Wiley [50]

determination of lysozyme in raw egg samples using sodium dodecyl sulfate as the reagent [49].

Lin et al. reported the use of wooden capillaries (WCs) instead of WTs or metallic capillaries (MCs) coupled to AIMS, giving birth to the WC-ESI-MS technique. The configuration of this technique is depicted in Figure 4. These WCs consist of a fused silica capillary inserted into the WC 1 mm away from the end of the tip of the WC and the other part of the capillary is connected to a syringe pump with a peek tube also connected to a T-junction. This last element is also connected to a high voltage supply with a clip. WC-ESI-MS presents higher intensities and allows higher flow rates and water content than MCs. As WCs are not electrically conductive when no solvent is applied, they can avoid easy discharges that may occur with MCs. In addition, WCs present a higher ionization efficiency and lower interferences related to electrolysis products [50].

Although most applications of wooden materials in microextraction involve WT-ESI-MS as the instrumental technique, the use of wooden materials in combination with chromatography [51] and direct infusion (DI)-MS [52] has also been reported.

2.4 | General application of WT-ESI-MS

Non-coated WTs, specifically made of birch and bamboo wood, have widely been used to analyze biofluids, environmental, and food samples by WT-ESI-MS. So et al. reported for the first time the use of non-coated WTs to determine ketamine and norketamine in urine samples. Using an internal standard was essential to correct the instrumental fluctuations due to the batch-to-batch irreproducibility of WTs and the variations in sample loading. The authors suggested using the peak height instead of the peak area to eliminate any possible peak tailing on the instrumental signal [39].

Yang et al. developed a rapid WT-ESI-MS analysis to determine pesticides, toxicants, date-rape drugs, and illicit additives in complex food samples, including liquid beverages, hot soup, powdered food, and viscous drink samples with a sample analysis of 2 min. The sampling step was adapted to the nature of the sample. For liquid and viscous samples, 1 cm of the WT was introduced in the sample for 10 s to absorb ca. 10 μL of the sample. For powder samples, each WT was immersed in methanol for 10 s and introduced in the sample, including a rubbing step, to adsorb ca. 0.2 mg of the powder [53]. The same group also reported using WTs for the analysis of neopterin and biopterin in urine samples, providing a fast and reliable analytical tool for the analysis of clinical samples [54].

Hu et al. compared the behavior of different WTs surface modifications toward the quantitation of cocaine in oral fluid [44], while Ng et al. developed a rapid WT-ESI-MS technique to detect and quantify different drugs of abuse in urine and oral fluid [55].

Wu et al. combined in vivo sampling of different parts of living plants for direct sampling of metabolites, avoiding the classic sample treatment: harvesting, grinding, extraction, and chromatographic separation [56]. The strategy consists of the puncturing on different parts of the living plant (flowers, leaves, stems, veins, and roots) with WTs where the analytes are absorbed, followed by the addition of the solvent and the application of a high voltage to form the ESI.

2.5 | WT-ESI-MS as an efficient tool for fingerprint quality analysis

Another application of WT-ESI-MS is the analysis of the quality of commercial pharmaceuticals and natural products with a high sample throughput.

Yang et al. reported for the first time the use of WT-ESI-MS as a fingerprinting tool for the quality assessment and control of herbal products to avoid possible counterfeits and tracking their origin from different producers with a high sample throughput. Also, different active components and trace degradation products from several formats of pharmaceuticals were analyzed, including tablets, capsules, granules, dry suspensions, suspensions, drops, and oral liquids [40]. This group also developed a WT-ESI-MS approach for the evaluation of the quality assessment and control of herbal preparation, distinguishing between expired products and locating their manufacturer origin [37]. Xin et al. reported the synergy between WT-ESI-MS and multivariate statistical analysis for tracing the supply chain of pharmaceutical suppliers. This

approach permitted the detection of significant differences in MS features instead of the identification of the compounds [41]. Other studies were related to the development of different approaches for the quality assessment and control of an herbal formula discriminating samples regarding its quality, stability, consistency, and differencing quality damaged ones [57], quality of herbal medicines in terms of origin and authenticity [46], and identification and quantitation of herbal adulterants from similar species [58].

WT-ESI-MS combined with multivariate analysis was described as a metabolite fingerprint tool for distinguishing between healthy and endometriosis patients by global metabolomic profiling [42]. Pereira et al., discriminated the origin of garlics by WT-ESI-MS and multivariate pattern recognition methods to control the garlic authentication and avoid frauds. This approach consists of the direct sampling by the penetration of garlics with pre-wetted WTs, reducing the time of analysis by eliminating the sample treatment steps (digestion and clean-up steps) that are laborious and time-consuming [59].

3 | WOODEN-BASED SORBENTS FOR THE ISOLATION OF COMPOUNDS FROM COMPLEX SAMPLES

Although bare WTs are commonly used, different surface modifications have been implemented to enhance the sorbent-analyte interactions, including silanization reactions [35,38,44], and coatings with molecularly imprinted polymers [43,60], composite [51], and polymers [52]. These new interactions with the target analytes permit the isolation of the analytes improving the selectivity (by the elimination of potential interferents) and sensitivity (by preconcentrating the analytes and/or reducing the ion suppression in the MS analysis) of the determinations.

The surface of WTs can be modified by a silanization reaction taking advantage of the hydrophilic surface provided by the hydroxyl groups of the partial cellulosic composition of wood. Deng et al. reported for the first time a silanization modification by introducing a double mix-mode interaction—hydrophobic interactions related to C_{18} groups and ion-exchange adsorption with positively charged quaternary amines. This surface modification permitted the selective extraction of perfluorinated compounds from environmental aqueous samples, blood, and milk samples, improving the sensitivity of the method in two orders of magnitude for the last two complex matrices [35]. The same group also reported a silanization modification of the surface of WTs followed by a subsequent modification of the silanized-WTs with a sulfonation reaction for the determination of fluoroquinolones and macrolide antibiotics. These WTs interact with the target analytes, which are secondary and tertiary amine groups, by reversed-phase adsorption regarding the alkylic chain of the coating and by ion exchange due to the negative charge of the sulfonated groups [38].

Molecularly imprinted polymers have also been used as coating phases for WTs, giving birth to molecularly imprinted polymer-coated wooden toothpicks (MIPCWTs), regarding their selectivity and the extraction enhancement toward target analytes. Huang et al. developed a MIPCWT based on the deposition of silicone-modified acrylate molecularly imprinted emulsions with the template molecules, followed by the removal of these analytes. This procedure permitted the selective extraction of malachite green and metabolites from aquatic products, including real-life tap water, river water, and fish samples with enrichment factors of three orders of magnitude [60]. Liu et al. also reported the use of MIPCWTs for the determination of trace macrolide antibiotics in complex food samples. This chemical selective coating provides extraction folds of 3, 2, and 1 orders of magnitude for drinking water, honey, and milk samples, respectively [43].

Other coating strategies are focused on the dip-coating technique. It implies the dispersion of a polymeric or nanocomposite precursor solution in which the wooden-based sorbent is immersed, followed by a drying step. This procedure establishes new interactions between the sorbent and the analytes. Karimiyan et al. used wooden sticks coated by a nanocomposite formed by graphene oxide and polyethylene glycol for the isolation of β-blockers from the human oral fluid. The combination of graphene oxide and polyethylene glycol added new interactions with the analytes, such as hydrogen bonds, and π-π interactions. In this case, after the extraction, the wooden sticks are eluted, and the eluates are finally analyzed by LC-MS/MS. The use of a chromatographic separation provides high selectivity levels with a sample throughput of four samples per hour [51].

Millán-Santiago et al. reported the use of polyamide-coated WTs for the extraction of methadone, cocaine, and methamphetamine in oral fluid samples by DI-MS. Nylon-6, a commercial polyamide, enhanced the interaction with the target analytes by hydrogen bonds and electrostatic interactions due to the amide group and the alkylic chain of the polymer, respectively [52]. The narrow size of the WTs permits their introduction in conventional LC vials that were used as extraction vessels (Figure 5) and the simultaneous extraction of several samples. The analysis of the eluates by DI-MS, avoiding the chromatographic separation, increases the sample throughput up to 22 samples per hour.

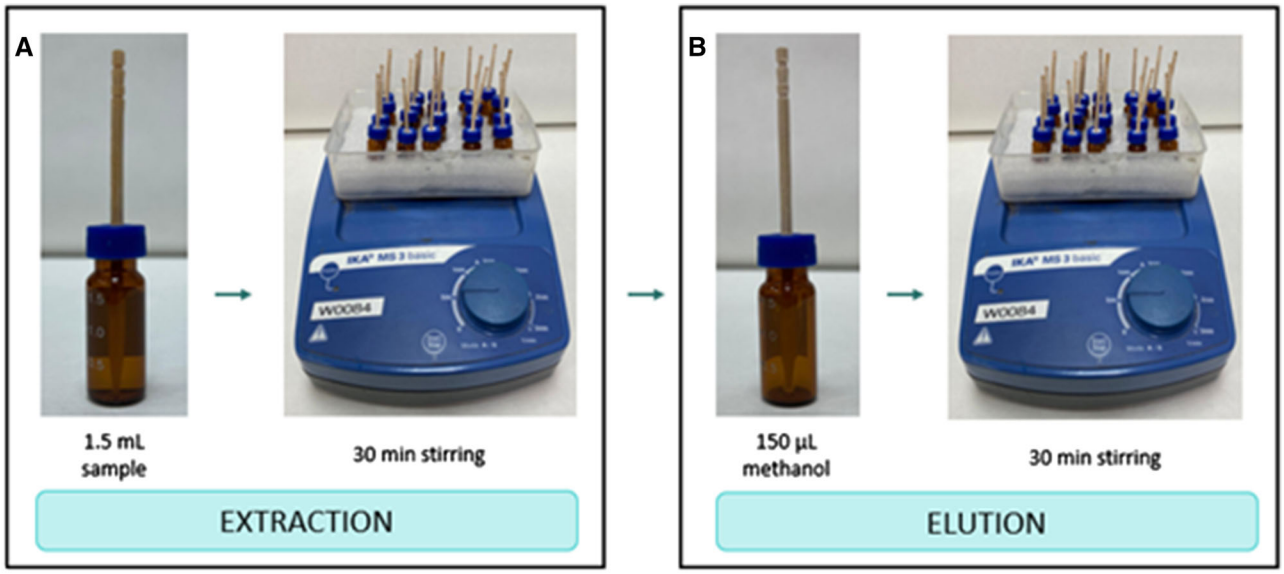

FIGURE 5 HPLC vials and inserts as extraction and elution vessels, allowing the simultaneous analysis of samples. Reproduced with permission from Elsevier [52]

4 | CONCLUDING REMARKS

SSMS techniques have been used in microextraction to design efficient and rapid analytical platforms. This combination avoids chromatographic separation and reduces drastically the sample treatment, providing shorter analysis times and lower consumption of organic solvents. The use of biosorbents is progressively increasing, providing a greener perspective to this microextraction context and fitting into the GAC and WAC guidelines. Consequently, the synergic blend of natural materials (in this case, wooden-based ones) and direct MS analysis is a hot topic in the analytical chemistry context. The description of the so-called WT-ESI-MS technique is a clear example of this synergy. However, the use of wooden-based materials is not limited to this technique, as some researchers reported their combination with LC-MS/MS and DI-MS/MS.

Non-coated WTs are mainly involved in sample deposition onto their tip followed by the sample analysis, whereas surface-modified wooden-based materials follow the classical SPME workflow: conditioning, extraction, washing, and elution steps. The increasing applicability of wooden materials includes the analysis of biofluids, liquid, slurry, and solid granulated samples, as well as the direct puncturing of solid samples with fingerprint quality analysis purposes, among other applications.

Wooden-based materials present some advantages over commercial sorbents. They are sustainable materials, and their use is in line with the GAC principles. They are cheap substrates that allow the design of multiple extraction devices. The composition of wood, containing cellulose and lignin as major components, opens the door to extracting analytes in a wide range of polarity. This extraction versatility can even be boosted by the easy chemical modification of the wood surface with different extraction groups. The shape and size of wooden tips make them attractive to the design of particular extraction workflows that minimize the eluent volume requirement. Also, the direct coupling of wooden tips to MS is an added value compared to conventional sorbents. However, an objective evaluation of the materials derived from our own experience also shows some limitations. Commercial wooden tips are not entirely batch-to-batch reproducible, and internal standards are mandatory to achieve an acceptable level of precision in the analytical determination. This issue becomes especially critical for WT-ESI-MS applications. Also, the materials must be cleaned before being used to remove endogenous compounds that may interfere in determining the target compounds.

ACKNOWLEDGMENTS

Financial support from the Spanish Ministry of Science and Innovation (PID2020-112862RB-I00) is gratefully acknowledged. J. Millán-Santiago expresses his gratitude for the predoctoral grant (FPU19/01488) from the Spanish Ministry of Science, Innovation, and Universities. Funding for open access charge: Universidad de Córdoba / CBUA. This article is based upon work from the National Thematic Network on Sample Treatment (RED-2018-102522-T) of the Spanish Ministry of Science, Innovation, and Universities, and the Sample Preparation Study Group and

Network supported by the Division of Analytical Chemistry of the European Chemical Society.

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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How to cite this article: Millán-Santiago J, Lucena R, Cárdenas S. Wooden-based materials: Eco-friendly materials for direct mass spectrometric analysis and microextraction. J Sep Sci. 2021; 1–10. https://doi.org/10.1002/jssc.202100660