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Potential of hydrophobic paper-based sorptive phase prepared by in-situ thermal imidization for the extraction of methadone from oral fluid samples

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ABSTRACT

Paper-based sorptive phases (PSPs) are functional planar materials with a demonstrated potential in analytical sample preparation. This article describes the synthesis of a polyimide coated paper by an in-situ imidization at a high temperature. Polyimides (PI) are synthesized in two subsequent steps where a hydrophilic polymer, in this case, poly(amic acid) (PAA), is formed as an intermediate product. PAA is finally transformed into hydrophobic PI by thermal curing at 180 °C. The synthesis of PI-paper takes advantage of this two-step procedure. In the first stage, a segment of filter paper is immersed into an aqueous PAA solution. After the solvent evaporation, the paper is heated at 180 °C for 1 h inducing the formation of the hydrophobic PI over the cellulose fibers. Infrared spectroscopy has been used to characterize the synthesized materials by defining a coverage factor F. The hydrophobicity of the materials has been studied using an aqueous methylene blue solution as a marker. To fully demonstrate the usefulness of the material in the sample preparation field, the extraction of methadone from oral fluid (OF) samples has been considered as a model analytical problem. The main variables affecting the synthesis (PAA concentration on the precursor solution and number of dips) and the extraction (elution and extraction times) have been fully evaluated. Working under the optimum conditions, a limit of quantification of 9 µg/L, intraday and interday precision better than 14.6%, and accuracy in the range of 87–108% were obtained.

1. Introduction

Planar sorptive phases are extremely useful in analytical sample preparation and they have been traditionally used, in the form of porous membranes and disks, in environmental analysis [1]. The potential of planar materials in microextraction has given rise to different techniques [2,3] that can be included under the thin film microextraction (TFME) concept [4]. Although some planar sorptive phases are commercially available, these materials can also be ad-hoc synthesized and adapted to a defined analytes/sample matrix combination, thus increasing their versatility. The preparation of planar sportive phases can be done following two general synthetic workflows. In the first one, a precursor material is transformed into a mat or thin film by using special techniques like electrospinning [5] or spin coating [6]. These techniques provide high-performance sorbents but require special manifolds to be developed. In the second approach, the materials can be obtained by directly modifying an existing planar substrate. This approach is used, for example, to prepare fabric phases [7–9], where cellulose fabric is typically modified by a sol-gel reaction to include the actual sorptive phase. The same strategy has also been reported to design paper-based sorptive phases (PSPs).

Paper is a planar cellulosic substrate that has been used in the laboratory for many purposes, including filtration or phases separation. Although commercial papers have different qualities (chromatographic, filter), they can generally be considered affordable and cheap materials, especially if compared with other ordinary laboratories supplies. The use of paper as a sorptive phase dates back to the 1990s when Chen and Hurtubise reported using com-

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mercial hydrophobic paper to extract polycyclic aromatic hydrocarbons [10]. Even then, the authors suggested the in-surface spectroscopic monitoring of the isolated analytes avoiding the elution step [11]. Other authors have further addressed this simple extraction workflow using spectrometric [12,13] and portable spectroscopic [14] techniques.

Cellulose paper is a hydrophilic material. Although it can be directly used to extract target compounds [15,16] its modification is usually preferred to improve the extraction capacity or modify the possible interaction chemistry with the analytes. Up to date, different strategies have been used to fabricate PSPs. The OH-rich surface of cellulose has been exploited for the covalent immobilization of sorptive groups, including aptamers [17], silanes [18], isocyanates [19] or amines [20]. Paper structure can also be used to host a solvent in the pores [21] and this impregnation can be improved by the thermal curing of the paper inducing a partially covalent binding [22]. Our research group has extensively used the physical deposition of a sorptive phase over the paper surface to synthesize PSPs using the dip-coating technique. In this approach, the paper is immersed into a precursor media that could be a polymer dissolved in an appropriate solvent [23–26], a nanomaterial dispersed in a solvent [27] or a polymer dissolved in a solvent containing dispersed nanomaterials [28]. After the dipping, the solvent is removed, and the paper is coated with a polymer, a nanomaterial or a polymeric nanocomposite, respectively, depending on the precursor media.

Polyimides (PI) are highly hydrophobic polymers that have already been used in fiber solid-phase microextraction [29], TFME [30], and bar adsorptive microextraction [31]. PI synthesis involves two consecutive but independent steps that are shown in Figure S1. In the first stage, a diamine and a dianhydride react to provide a still water-soluble poly(amic acid) (PAA). This intermediate is transformed into a water-insoluble PI by thermal curing that creates new imide cycles in the structure [32]. Ma et al. have recently proposed the synthesis of a support-less PI membrane for the TFME of organochlorine pesticides (OCPs) with excellent results [30]. For this synthesis, the authors designed a special chamber. We hypothesized that the experimental conditions for the synthesis of PI are fully compatible with paper. This article reports the synthesis of a PI-paper, which consists of the preliminary synthesis of the PAA, the dipping of paper into this solution, and the final thermal curing to induce the in-situ imidization. The resulting material renders a hydrophobic character, and its potential has been evaluated using the determination of methadone (MTD) in oral fluid (OF) samples as the model analytical problem. MTD is a synthetic opioid that can be used to treat chronic pain or opioid dependence. Methadone maintenance treatment (MMT) programs are exploited to treat opioid dependence since the 1950s, however, MTD might be diverted from the licit to the illicit drug market, thus increasing the risk for methadone-related overdoses. To ensure drug safety and effective treatments, the concentrations of MTD in biological matrices should be carefully controlled by highly reliable protocols featuring low invasiveness and high subject compliance.

At physiological pH values, MTD is non-polar, although the hydrophobicity can be boosted at basic pH, reaching values of the logarithm of octanol/water partition coefficient up to 5. Its practical interest [33] and hydrophobic character make MTD interesting to evaluate the extraction performance of the PI-PSP from OF.

2. Experimental section

2.1. Chemicals and solutions

MTD hydrochloride and HPLC grade methanol (MeOH) were purchased from Sigma Aldrich (Madrid, Spain). A stock solution of the analyte was prepared at the concentration of 1000 mg/L in MeOH. The working solutions were daily prepared in MeOH or Milli-Q water (Millipore Corp., Madrid, Spain), starting from the stock solution, depending on their final use.

Pyromellitic dianhydride (PMDA), 4,4′-oxydianiline (ODA), tetrahydrofuran (THF) and triethylamine (TEA) were used for the synthesis of PAA. These reagents were also purchased form Sigma Aldrich.

Blank OF samples were acquired using a Salivette® device. The cellulose pad is introduced into the oral cavity and chewed for 60 s, collecting the OF which is finally recovered by centrifugation. These blank samples were used during method validation where the absence of analytes in the sample is required. However, the retention of some drugs in cellulose pads has been reported by Sobczak and Goryński [34], and therefore the spitting process is recommended for collecting real samples.

2.2. Synthesis of the polyimide coated paper-based sorptive phase (PI-PSP)

2.2.1. Synthesis of the PAA polyimide precursor

The synthesis of PAA has been performed following the procedure reported by Andreescu *et al.* [35]. 0.10 mol of the two monomers (ODA and PDMA) were solubilized in 50 mL and 20 mL of THF, respectively, using two different flasks. After complete solubilization of the monomers, the PDMA solution was added in the ODA solution over 40 min under continuous stirring. Then 35 mL of MeOH containing 0.02 mol of TEA were added drop by drop with a burette and the mixture was stirred for 24 h.

The obtained mixture presented a yellow solution and a little brown gel that was the PAA. 2 g of the gel was solubilized in 10 mL of water. The gel contains both PAA and solvents, so the actual concentration of this solution was precisely evaluated. For this purpose, 1 mL of the solution was thermal cured at 180 °C for 1 h and the resulting solid residue (PI) was weighted. The results showed that the solution present a PAA concentration of 10% (w/v). This concentration is expressed as the potential amount of PI that can be obtained after the thermal curing by the process of imidization at 180 °C.

2.2.2. PAA coating and thermal curing

For the preparation of PI-PSP the precursor solution was diluted to a 3% (w/v). A segment of paper (1 × 3 cm) was dipped in this solution and the solvent was evaporated using a heat gun. The dried paper was subsequently heated at 180 °C for 1 h to transform the PAA into PI. To achieve a more homogeneous coating of the paper, the paper was dipped twice into the solution changing the immersion direction. The parameters involved in the synthesis of the PI-PSP (solution concentration and number of dips) were properly optimized by evaluating MTD extraction from aqueous standards. For doing so, the PI-PSPs were incubated with 5 mL of an aqueous standard containing MTD at 0.10 µg/L, under continuous agitation at 750 rpm for 30 min. For the elution, the paper was introduced in a 200 µL pipette tip and eluted with 100 µL of MeOH.

2.3. Characterization of the materials

The PAA, the PI and the modified papers were characterized with different techniques. The attenuated total reflection infrared spectroscopy (ATR-IR) spectra of each sample were acquired with a Bruker Tensor 37 FT-IR spectrometer (Bruker Optik, GmbH, Ettlingen, Germany) equipped with a three internal reflections diamond ATR cell (Platinum ATR accessory, Bruker). The modified papers were also characterized by the scanning electron microscopy (SEM) at the central Service for Research Support (SCAI) of the

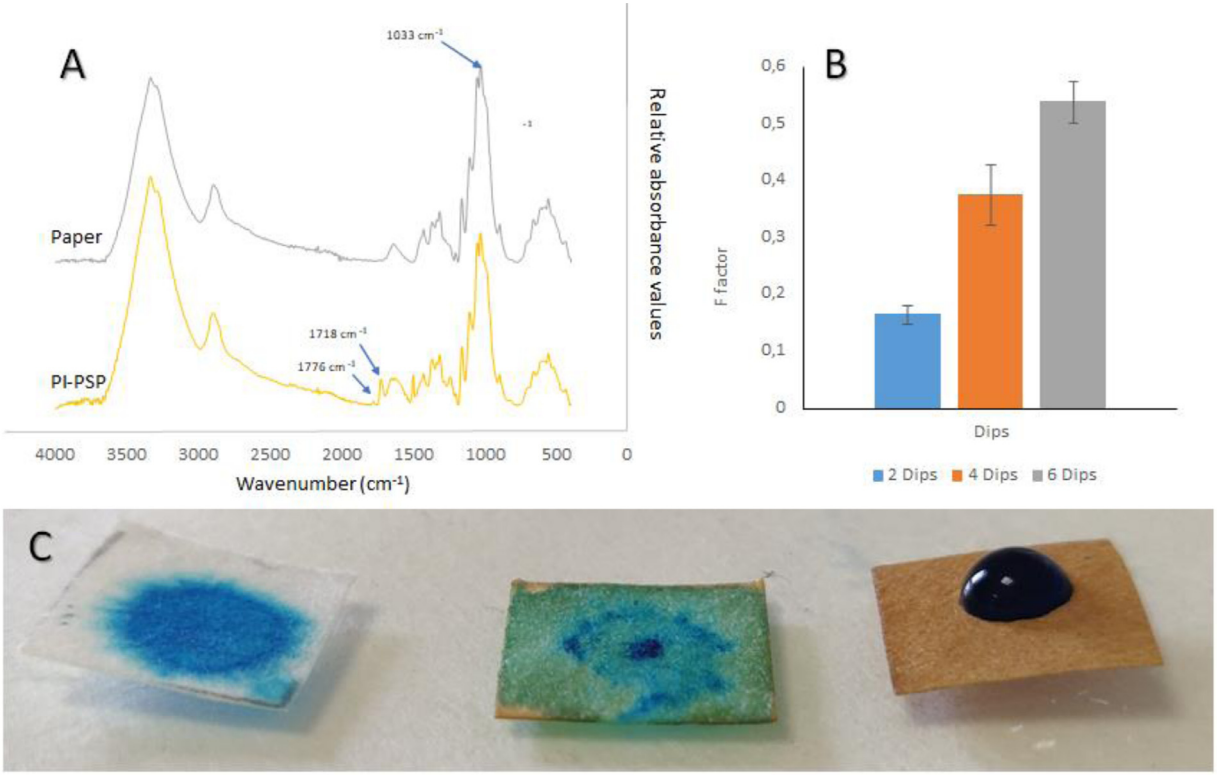

Fig. 1. A) ATR-IR spectra of pure paper and PI-PSP. B) Influence of the number of dips on the F factor. C) Pictures of pure paper (left), PAA-paper (center) and PI-PSP immediately after the deposition of a drop of an aqueous solution of methylene blue.

University of Córdoba using a JEOL JSM 7800F microscope (JEOL, Tokyo, Japan).

The hydrophobicity of the materials, that can be considered as a marker of the imidization process, was qualitatively evaluated using an aqueous solution of methylene blue.

2.4. Extraction procedure from OF samples

A 5 mL OF sample (diluted 1:2 with Milli-Q water and adjusted to pH 10 with a sodium hydroxide solution) was placed in an extraction vial where a PI-PSP was introduced. The vial was stirred at 750 rpm for 120 min in an orbital shaker where several samples can be extracted simultaneously. After the extraction, the PI-PSP was removed from the vial, washed with Milli-Q water and placed into a 200 µL-pipette tip where the elution was developed. This elution was done by pipetting 15 times the same volume of 100 µL of methanol. The eluate was finally analyzed by GC–MS.

To avoid cross-contamination and to reduce the solvent consumption (required to washing the PI-PSP), fresh PI-PSP were used for each extraction.

2.5. GC–MS analysis

The instrumental analysis was carried out on a HP6890 gas chromatograph (GC) coupled with an HP5973 mass spectrometer from Agilent (Palo Alto, CA, USA). The GC was equipped with a HP-5MS column (30 $m \times 0.25$ mm I.D. $\times 0.25\ \mu$m film thickness) using Helium (6.0 grade purity, Air Liquid, Seville, Spain) at a flow rate of 1 mL/min as the carrier gas. The column temperature program was as follow: 90 °C for 1 min; raised to 240 °C at 40 °C/min, maintaining this temperature for 5 min and finally increased to 280 °C at 40 °C/min. The injector was set at 160 °C, and a splitless mode injection was selected. Electron impact ionization (70 eV) was used for the ionization and fragmentation of the analytes. The MS was setting on selecting ion monitoring (SIM) mode using a *m/z* value of 72 for MTD monitoring. The MS source and quadrupole temperatures were 230 °C and 150 °C, respectively.

2.6. Validation of the method

All validation parameters were calculated based on the FDA international guidelines.

2.6.1. Calibration curve and sensitivity

For the calibration curve, spiked samples of OF at seven different concentrations (0.02, 0.10, 0.20, 0.30, 0.50, 0.80, 1.00 mg/L) were analyzed after being submitted to the developed extraction procedure. Every concentration was analyzed three times and the mean values were used for the construction of the calibration curve. The sensitivity was calculated in terms of limit of detection (LOD) and limit of quantitation (LOQ), in accordance with the FDA guidelines.

2.6.2. Precision

The precision was evaluated as intraday and interday precision at three different concentrations (0.02, 0.50 and 1.00 mg/L). The intraday precision was expressed as the precision of three analyses repeated in the same day and the interday precision as the precision of three analysis repeated in three consecutive days. The data were expressed in terms of relative standard deviation (RSD) and considered satisfactory for values lower than 15%.

2.6.3. Accuracy

For the evaluation of the accuracy, spiked OF samples at three different concentrations (0.02, 0.50 and 1.00 mg/L) were analyzed in triplicate and the relative MTD concentrations were calculated. The accuracy values were expressed as the% of correlation with the real concentration. The results were considered good into the range 85–115%.

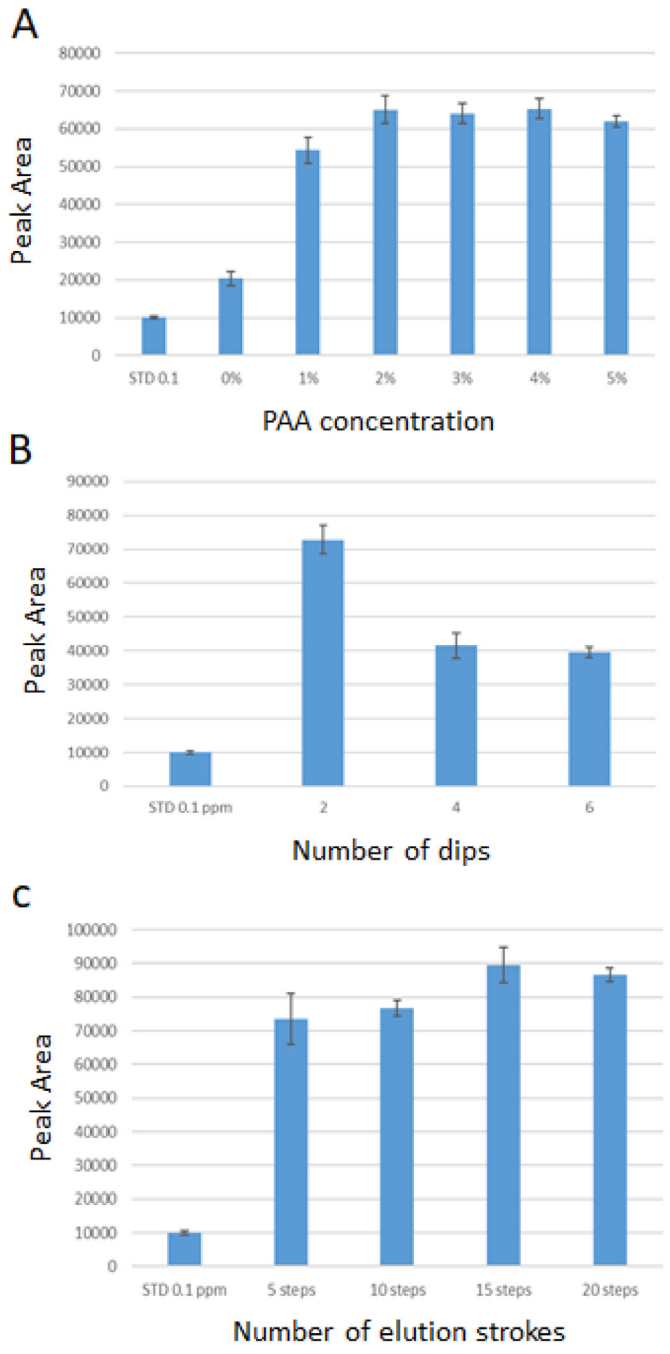

Fig. 2. A) Effect of the PAA concentration used in the precursor on the extraction ability. B) Effect of the number of dips on the extraction ability, C) Effect of the number of elution strokes. The signal obtained for the direct injection of a methanolic standard containing the analyte at 0.1 mg/L (STD 0.1 ppm) is included for comparative purposes.

3. Results and discussion

3.1. Characterization of the materials

Infrared spectroscopy was used to chemically characterize the materials. First, the spectrum of PAA was obtained by depositing the aqueous solution of the PAA gel over the ATR element and letting the solvent evaporate (Figure S2). The PI, obtained by the thermal imidization of the PAA, was also measured. The PI spectrum was acquired placing a few mg of the solid over the ATR and applying pressure (Figure S2). As it can be observed in Figure S2, two bands at 1776 and 1718 cm^{-1} appear after the imidization. These bands can be ascribed to the asymmetric and symmetric vibrations of the cyclic imide carbonyl group, and they are in accordance with the studies reported on the literature [36,37]. The IR spectrum of paper is shown in Fig. 1A and presents an intense absorption band at 1033 cm^{-1} which is ascribed to the C–O-C pyranose ring vibration. The IR spectrum of the PI-PSPs shows (Fig. 1A), together with the absorption bands of cellulose, two bands at 1776 and 1718 cm^{-1} that confirm the successful immobilization of PI on the paper support.

Table 1
Results of the precision (intraday and interday) and accuracy study.

MTD OF conc. (mg/L)	Intraday precision (RSD%)	Interday precision (RSD%)	Accuracy (%)
0.02	3.0	7.1	95.3
0.5	14.6	11.8	107.8
1	7.1	12.0	86.9

According to our experience, the ATR-IR spectra of modified papers are hardly quantitative because it is highly affected by the pressure applied during the spectrum acquisition. In fact, the intensities obtained for the same paper at the same point can be different in consecutive measurements although the shape (absorption ratio at different wavelengths) remains. To study the homogeneity of the paper coating, a F factor was defined. This factor is the ratio of the absorbances at two different wavenumbers, namely: 1718 cm^{-1} (characteristic absorption band for PI) and 1030 cm^{-1} (characteristic absorption band for cellulose). The ratio is not affected by the pressure applied during the measurements and it is proportional to the PI coating. The penetration depth of the diamond ATR is in the range 1–2 µm depending on the wavenumber. A naked paper should give a F of 0.011 which is the value practically calculated using the spectrum of pure paper. A paper with a PI coating thicker than 1–2 µm should provide a F of 8.33 which is the value practically calculated using the spectrum of pure PI. Fig. 1B shows the F factors obtained for papers coated with different layers (2, 4 and 6) of PI. As described in Section 2.2.2 an even number of immersions is preferred to obtain a more homogeneous coating. As expected, the F increases with the number of PI layers. The calculated F shows a partial coating of the papers since the values are far from the 8.33 reference. These values are the average of six independent measurements of the same paper in different positions. The low standard deviation of the measurements, represented as the error bars in the graphs, also demonstrates that the coating is homogeneous.

Cellulose and PAA are hydrophilic polymers while PI is hydrophobic. The hydrophobicity of the PI-PSP can be used as a marker of a successful imidization. The hydrophobicity of the papers was studied using an aqueous solution of methylene blue. Fig. 1C shows the picture of paper, PAA-paper and PI-paper immediately after the deposition of a 15 µL-drop of the methylene blue solution. The drop is visible and stable in the PI-paper demonstrating its hydrophobic character while the solution easily diffuses over the surface of pure paper and PAA-paper. Figure S3 shows the pictures of the papers after the complete evaporation of the drops. The diameter of the spot generated on the PI-paper was 0.4 cm, smaller than both the blank paper (0.7 cm) and the PAA paper (0.6 cm). This spot diameter can also be used as a hydrophobicity marker.

According to the F factor study, the papers are partially coated with PI. This aspect involves that the cellulose core is also partially exposed to the solutions placed over the paper. The hydrophobicity of the PI-papers of different layers (2, 4 and 6) was studied by depositing 5 µL of water and measuring the time required for the drop disappearance. The tests were carried out at the same con-

Table 2
Comparison of the proposed method with other recently reported in the literature facing the same analytical problem.

Sample	Extraction technique	Instrumental technique	LOD[1] (μg/L)	RSD[2]	Accuracy[3]	Reference
Saliva	Paper-based soprtive extraction	GC–MS	3	< 14%	106% (RR)	[23]
Dried saliva	Dried saliva spots sampling	GC–MS/MS	5	<10.99%	1.04–10.9% (RE)	[33]
Saliva	Dispersive solid phase extraction using layered double hydroxide intercalated with tyrosine	GC–MS	0.5	< 7.5%	72% (RR)	[38]
Saliva	ultrasound energy assisted solidification of floating organic drop microextraction	GC–MS	0.7	<6.8%	93.1–97.7	[39]
Saliva	Ultrasound-Assisted Dispersive Liquid-Liquid Microextraction	GC/MS	50	5.2–11.3%	89.4–115.5% (RR)	[40]
Saliva	Paper-based soprtive extraction	GC/MS	3	<14.6%	86.9–107.8% (RR)	This paper

[1] LOD, limit of detection.
[2] RSD, relative standrd deviation.
[3] RR, relative recovery. RE, relative error.

ditions of temperature and humidity. The disappearance depends on two simultaneous processes, namely the water evaporation and the slow diffusion of the drop through the partially covered surface to the cellulose substrate. The drop of water needed 30 s, 60 s and 210 s to disappear on the surface of the papers synthesized with 2, 4 and 6 layers respectively. This study confirms that the hydrophobicity of the papers depends on the number of PI layers.

The SEM images of the blank paper, PAA-paper and PI-paper are shown in Figure S4. The pictures only show subtle differences probably due to the partial coating.

3.1.1. Effect of the PAA concentration in the precursor solution

The concentration of the PAA precursor solution was evaluated at six different levels, namely: 0%, 1%, 2%, 3%, 4% and 5%. The results are presented in Fig. 2A where they are compared with the signal provided for a methanolic MTD standard at 0.10 mg/L to evaluate the preconcentration ability. According to the results several conclusions can be inferred. Firstly, the extraction ability increases with the PAA concentration up to 2–3% which corroborates the active role of PI on the extraction of MTD. Although pure paper (0% of PAA) also extracts the analyte in a lesser extent, this interaction used to be more sensitive to the matrix effect according to our previous experience. A concentration of 3% was selected as the optimum value for further studies.

3.1.2. Effect of the number of dips

Once selected the concentration of the PAA in the precursor solution, the number of dips defines the coating thickness of the paper support. Different even numbers of dips (2, 4 and 6) were used to prepare different PI-PSP and the extraction capability of each one was evaluated. The results, that are shown in Fig. 2B, indicates that the extraction capability of the PI-paper is reduced by increasing the number of dips. This behavior seems inconsistent with the active role of PI on the extraction of MTD, but it has been observed for polymeric coated papers. This effect can be explained by two different reasons. On the one side, for lower number of dips, the PI is formed over the cellulose fibers exploiting their high superficial area. A larger deposition can partially block the pores reducing the superficial area. On the other side, a larger deposition can maximize the hydrophobicity of the paper surface minimizing its wettability in an aqueous media. A compromise between hydrophobicity and wettability is therefore required. According to the results, 2 dips were selected as the optimum value.

3.2. Optimization of the extraction

The next parameter considered for the optimization of the extraction procedure was the number of strokes required for the MTD elution from the PI-paper. MeOH was selected as a solvent and four different number of strokes (5, 10, 15 and 20 strokes) were applied. MTD signal (Fig. 2C) increases with the number of strokes up to 15, which was finally selected as the optimum value.

Four different extraction times (30, 120, 180 and 240 min) were tested. The results (data not shown) indicated an increase of the extraction yield from 30 to 120 min without a significant increase for longer times. Also, the precision decreases for larger extraction volumes.For this reason, 120 min was selected as the optimum extraction time. This extraction time does not affect critically to the sample throughput since several samples can be extracted simultaneously in an orbital shaker.

3.3. Validation of the method

Blank OF samples spiked at seven different concentrations were subjected to the developed extraction procedure and analyzed by GC–MS. A model chromatogram is shown in Figure S5. A satisfactory linearity (R^2=0.9943) was observed in the range of MTD concentration of 0.02 – 1.00 mg/L in OF. The LOQ resulted to be 9 μg/L.

The precision was evaluated in terms of intraday and interday precision. Spiked OF samples at three different concentrations (0.02, 0.50 and 1.00 mg/L) were pretreated by means of the developed extraction procedure and then analyzed by GC–MS. This analysis was performed three times in the same day for the intraday precision and three times in three different days for the interday precision. The values were calculated as RSD% of the signal showing satisfactory results (always < 14.7) for each concentration (Table 1).

For the accuracy, spiked samples of OF at three different concentrations (0.02, 0.50 and 1.00 mg/mL) were pretreated with the developed extraction procedure and analyzed by the GC–MS method. For each sample the MTD concentration was calculated and used to evaluate the accuracy, expressed as the% of correlation with the real concentration. This analysis was repeated three times for each concentration and the mean values with relative errors were calculated. The satisfactory results obtained, with the values in the range of 86.9–107.8, have proved the good accuracy of the methodology (Table 1).

Table 2 compares the performance of the proposed method with other recent counterparts facing the determination of methadone in saliva by GC–MS [23, 33, 38-40]. The new approach is competitive with other approach in both sensitivity and accu-

racy. Although the precision is acceptable for a bioanalytical application, the use of an internal standard would be required for better data reproducibility.

Conclusions

This article reports a new synthesis approach for preparing paper-based sorptive phases (PSPs) where filter paper is used as substrate to deposit a polyimide coating avoiding the use of special synthetic approaches (e.g., casting, spin coating). This approach combines the dip-coating technique using an aqueous polymeric solution as a precursor followed by thermal curing to form a stable and hydrophobic polymer on the paper finally. Considering the IR spectra, a partial coating of the cellulose fibers is obtained, which permits exploiting the superficial area of the substrate. The polymeric coating improves the inherent sorption capacity of raw paper to extract MTD, which has been selected as the model analyte. In this sense, the extraction capacity increases with the concentration of PAA in the precursor solution up to 3%. At this PAA concentration, the number of dips reduced the sorption capacity. This phenomenon has also been reported for other polymeric-coated papers. In further studies, the combined effect of the percentage of PAA and the number of dips will be considered in detail.

The performance of the hydrophobic paper in a sample preparation workflow has been evaluated, and the resulting analytical method allows the determination of MTD in OF samples with good validation data. The development of a functionalized PSP can pave the way for affordable pretreatment approaches and analytical platforms for an effective and feasible assessment of MTD in OF samples, to be applied in forensic purposes and to monitor subject adherence to MMT regimens. The versatility of polyimides, which can be synthesized using monomers with different structures, is also an interesting aspect for future works.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Marco Cirrincione: Investigation, Data curation, Writing – original draft. **Rafael Lucena:** Conceptualization, Supervision, Writing – review & editing. **Michele Protti:** Supervision, Data curation, Writing – review & editing. **Laura Mercolini:** Supervision, Data curation, Writing – review & editing. **Soledad Cárdenas:** Supervision, Funding acquisition, Project administration, Writing – review & editing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2022.463166.

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