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Construction and evaluation of a flow injection micro-analyser based on urethane–acrylate resin

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ABSTRACT

A flow injection micro-analyser with an integrated injection device and photometric detection is described. Channels measuring 205–295 μm depth by 265–290 μm maximum width were manufactured by deep UV lithography on two layers of urethane–acrylate oligomers-based photoresist. Hypodermic syringe needles (450 μm diameter) were connected to the channels for introduction of solutions into the system. Plastic optical fibres were connected to the ends of a 5.0 mm long channel, in order to conduct the light from and to a homemade photometer. The device has a total volume of 7.0 μL and three different sample volumes (0.09, 0.22 and 0.30 μL) can be inserted into the system by choosing the appropriate loop of the hydrodynamic injection approach. The micro-analyser, designed as a single line manifold, was evaluated by determining chloride in waters (mercuric thiocyanate method), and chromium (VI) in wastewater and total chromium in metallic alloys (diphenylcarbazide method). For chloride determination two micro-pumps were employed to impel the solutions, while for chromium determination this task was performed by a conventional peristaltic pump. The results obtained in all determinations did not differ significantly from the reference methods at a confidence level of 95%. In the chloride determination, a flow rate of 50 μL min^{-1} was used, providing a sample frequency of 45 injection h^{-1}, generating ca. 0.7 mg of Hg(II) after an 8-h working day (ca. 20 mL of solution). This result suggests the potential of the micro-analyser towards the reduction of waste, following the philosophy of Green Chemistry.

1. Introduction

Nowadays, the miniaturisation of systems for chemical analysis is one of the dominant themes in analytical instrumentation. The major interest of the scientific community in miniaturised systems relates to their characteristics, such as portability, low reagent consumption and reduction of analysis time, which reduce the operational costs and the generation of residues.

Since the introduction of the concept of micro-Total Analytical Systems (μTAS) in the early 1990s [1], the well-established techniques of the semiconductor industry have been widely employed for the fabrication of microfluidic devices in silicon, glass and quartz [2]. In most of the cases, these techniques and materials require special conditions, such as clean-room facilities and highly concentrated reagents, which make production expensive and unsuitable for fabricating micro-systems in ordinary laboratories.

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More recently, great effort has been dedicated on simpler techniques [3] for manufacturing microfluidic devices using different kinds of polymers. It was demonstrated that, depending on the polymer characteristics, a prototype of an analytical micro-system can be made in a few hours, presenting acceptable performance for a series of applications. Lee et al. [4] reported the construction of a microfluidic device in solid poly(methylmethacrylate) (PMMA) using hot embossing, in which a mould made in silicon or a Ni–Cr wire was pressed against the surface of the substrate, under a controlled temperature, to create the channels of the system employed for separation and detection of DNA fragments. Yamada and Seki [5] made, by injection moulding, a nanoliter-sized liquid dispenser array for multiple biochemical analysis in microfluidic devices based on polydimethylsiloxane (PDMS). In this procedure, the PDMS pre-polymer and the curing agent were mixed and poured onto a negative master made in silicon. After curing in an oven at 90 °C for 30 min, the PDMS was completely polymerised and peeled off from the master.

The literature shows that although these simple technologies have been widely employed to develop microfluidic systems for applications in bioanalytical and clinical analyses that use electrophoresis [6], their use for the development of micro-Flow Injection Analysis (μFIA) is not generalised. Conventional FIA analysers have been developed and successfully applied over the past 30 years, providing a simple way of automating many manual wet chemical analytical procedures [7–9]. Although these systems present good performance in terms of analytical throughput and reagent consumption, their miniaturisation provides further improvement in their performance, with results similar to those obtained with larger scale devices. Rainelli et al. [10] developed a miniature flow injection analysis manifold in solid PMMA, whose channels were produced by micromilling, measuring 150 μm depth by 180–360 μm width. With the use of syringe pumps to propel the solutions, the prototype was applied to the photometric determination of iron, chloride and nitrite, performing 5 determinations h^{-1} with the consumption of 10 μL min^{-1} of sample and reagents. Greenway and co-workers [11] described the fabrication of a micro-flow injection analysis system, by wet etching borosilicate glass [2] and employed it for the determination of nitrate. A miniature column containing immobilized cadmium was placed in the sample reservoir of the device, acting as a reducing agent. The solutions were propelled by electro-osmotic flow (EOF) and the detection was performed by a micro-spectrometer, providing a detection limit of 0.50 μmol L^{-1} and an analytical throughput of 30 samples h^{-1}. Leach et al. [12] proposed a microfluidic FIA system made on PDMS, which integrates peristaltic pumps, sample loop, a mixing column and a transparent window for fluorescence detection. The system allows the injection of sample volumes of 1.25 nL, with a relative standard deviation of 3%, and an analytical frequency greater than 60 samples h^{-1}. Wang and Pumera [13] described a micro-FIA system for determination of trinitrotoluene, using a commercial glass chip, with a four-way injection cross. Fluids were impelled by means of electrophoretic flow, allowing 150 assays h^{-1}, and the amperometric detector provided a detection limit of 7.0 μg L^{-1} for TNT, with a relative standard deviation of 2.0%.

The present work describes the development of a micro-FIA system with integrated sample injection device and photometric detection. A simple and inexpensive technique of fabrication, recently introduced by Fernandes and Ferreira [14], was used and optimised in order to imprint channels in a polymeric substrate by deep UV lithography as well as making the sealing of the system. For the evaluation of the performance of the micro-analyser, the determinations of chloride and Cr(VI) ions using well-established photometric methods [15] were carried out.

2. Experimental

2.1. Apparatus

A commercial photoexposer machine (Fotolight-MD2-A4, Carimbos Medeiros Ltda, Brazil), with two sets of four mercury lamps (black light F15W T12 Sylvania), was used to perform the exposure of the substrate to UV radiation. The photomasks were designed with the aid of AutoCad-2002 software (AutoDesk) and printed on an overhead transparency at a resolution of 1200 dpi with a laser printer (HP LaserJet 1300). An ultrasonic bath (Branson model 2210) was employed in the development step of the exposed substrate.

To propel the solutions, miniature variable volume pumps, models LPVX 0502150 B (250 μL full stroke) and LPVX 0504950 B (750 μL full stroke), were purchased from Lee Company, presenting resolutions of 0.5 and 1.5 μL, respectively, in the full-step operation mode. These pumps also work in the half step mode, allowing insertion of half of the above volumes in each step. A peristaltic pump (Ismatec model ISM 931) was used to propel the solutions for the determination of chromium. Mini solenoid valves (model LHDA 0531415H), also acquired from Lee Company, were used to control flow directions.

Software to control all the operations of the micro analyser and for data acquisition through a parallel interface PCI-9111DG/HR (Adlink Tech. Inc.) was written in Microsoft VisualBasic 5.0.

For comparison with the results obtained with the μFIA system, an UV/vis spectrophotometer (Jenway 6405) was employed to determine Cr(VI) in contaminated underground waters and total chromium in Ni–Cr alloys as well as for the determination of chloride in mineral waters.

2.2. Reagents and solutions

The urethane–acrylate photoresist was acquired from Carimbos Medeiros Ltda (Macdermid, trademark Flexlight M050).

Analytical grade reagents and distilled/deionised water were used to prepare all solutions.

For the determination of chloride, reference solutions from 0.0 to 10.0 mg L^{-1} were prepared by proper dilution of a 1000 mg L^{-1} chloride stock solution, prepared with sodium chloride (Synth). A solution containing 2.0 mmol L^{-1} Fe(III) and 0.5 mmol L^{-1} $Hg(SCN)_2$ was prepared by dissolving the appropriate amounts of $Fe(NO_3)_3{\cdot}9H_2O$ (Vetec) and $Hg(SCN)_2$ (Merck). Commercial mineral waters were acquired in the local market and appropriately diluted with deionised water. The

pH of all solutions was adjusted to 4.0 by using an appropriate volume of concentrated HNO_3 (Merck).

For chromium determination, a 1000 mg L^{-1} stock solution was prepared by dissolving the appropriate amount of potassium dichromate (Vetec) in water. Cr(VI) reference solutions in the concentration range from 0.0 to 1.5 mg L^{-1} were prepared by the proper dilution of the stock solution. A 0.05% (m/v) diphenylcarbazide (Vetec) solution and a 0.8 mol L^{-1} H_2SO_4 (Synth) solution were used as reagents. Ni–Cr alloys (200 mg) were dissolved in aqua regia (25 mL) and the resulting solutions were treated with sodium persulfate (1.5 g) at 80 °C for 20 min. Afterwards, the final volume of each solution was adjusted to 100 mL with a 0.5 mol L^{-1} HCl solution, followed of proper dilution for measurements. Chromium (VI) contaminated underground water samples were supplied by the Environmental Chemistry Laboratory of Unicamp and prepared as recommended by a standard method [15].

2.3. *Construction of the micro-analyser*

The photolithographic process introduced by Fernandes and Ferreira [14] was the basis for manufacturing the micro-analyser. The fabrication procedure was improved in order to make possible the sealing of the channels without using any other material except the own urethane–acrylate resin. As shown in Fig. 1, the liquid photoresist was initially spread over the photomask (Fig. 1b) in a mould constructed with an acrylic plate and a rubber frame (Fig. 1a), which defines the thickness (2.0 mm in this work) and the shape of the polymeric film. Another acrylic plate (Fig. 1c) was used to close the plate set with the assistance of appropriate clamps.

The channels were engraved by exposing the photoresist to UV radiation in two steps. In the first step (Fig. 1d), the exposure was made for 75 s (360 mJ cm^{-2} dose) from the side without the shadow of the mask on the polymer. This step was necessary to create the bottom of the channels. In a second step (Fig. 1e), the other side of the plate set was irradiated for 85 s (410 mJ cm^{-2} dose), imprinting the mask design onto the photoresist. As the photoresist is negative [2], the regions below the printed areas of the mask did not polymerise, being removed with a commercial aqueous detergent solution (5%, v/v), with the aid of sonication in an ultrasonic bath for 10 min. In order to seal the channels, a top cover with thickness of 2.0 mm was cast by the same procedure described above, where the photoresist enclosed in the acrylic plate set was exposed for 135 s (dose of 650 mJ cm^{-2}) without the photomask. This top cover layer and the channels bottom layer were joined together by simple contact of the surfaces and then exposed to UV radiation for 20 min (dose of 5.8 J cm^{-2}). This exposure was performed under a nitrogen flow, providing an irreversible adhesion of the plates. Fig. 2 illustrates a scheme of the whole process of fabrication.

Hypodermic needles (305111 – BD™) with external diameters of 0.45 mm were coupled to the channels previously engraved in the polymeric substrate, to access the system. In a similar way, plastic optical fibres (250 μm diameter, Toray, UK) were coupled to the manifold and were employed to guide the radiation from a light emitting diode (LED) to the integrated flow cell (5.0 mm pathlength) and from the cell to the detector (photodiode RS 308-067) of a homemade photometer [16].

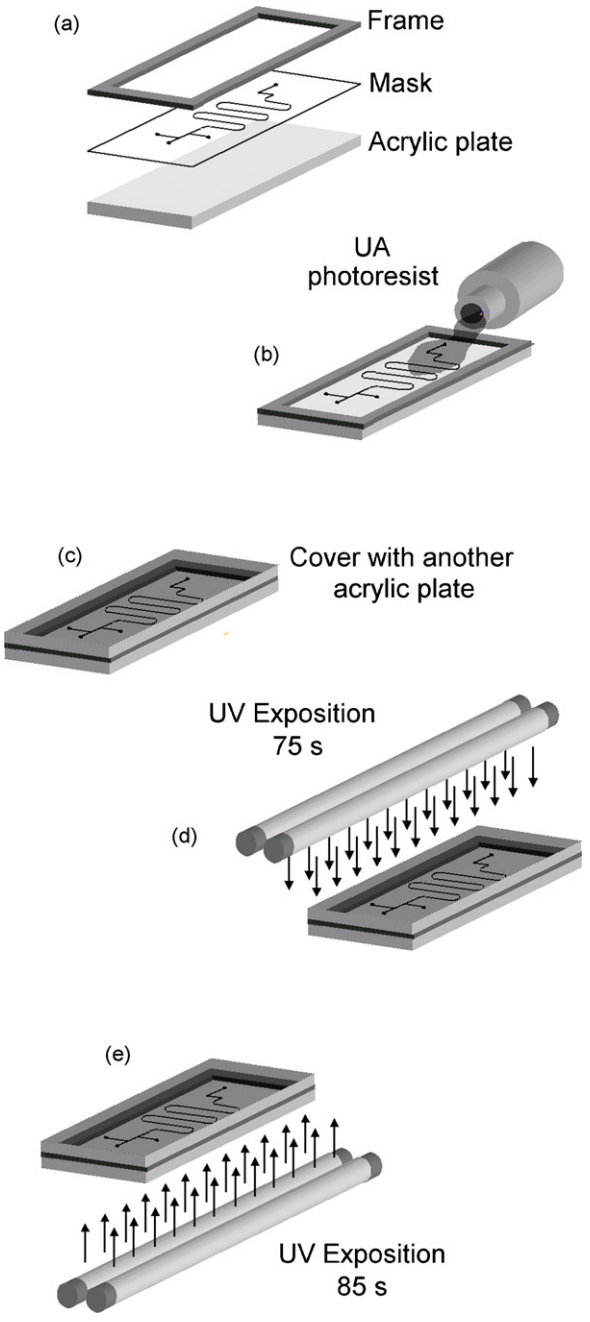

Fig. 1 – Schematic diagram illustrating the procedure for the construction of the micro-analyser. (a) assembly of the mould with the photolithographic mask, (b) deposition of the pre-polymer resin, (c) closing of the unit, (d) exposure during 75 s, (e) exposure during 85 s.

To prevent light scattering, both fibres were coupled directly to the detection channel as they are resistant to the chemical solutions used in the determinations of chloride and Cr(VI) ions.

2.4. *Procedures*

For the determination of chloride in mineral waters, measurements were carried out in a single-line flow system, as shown

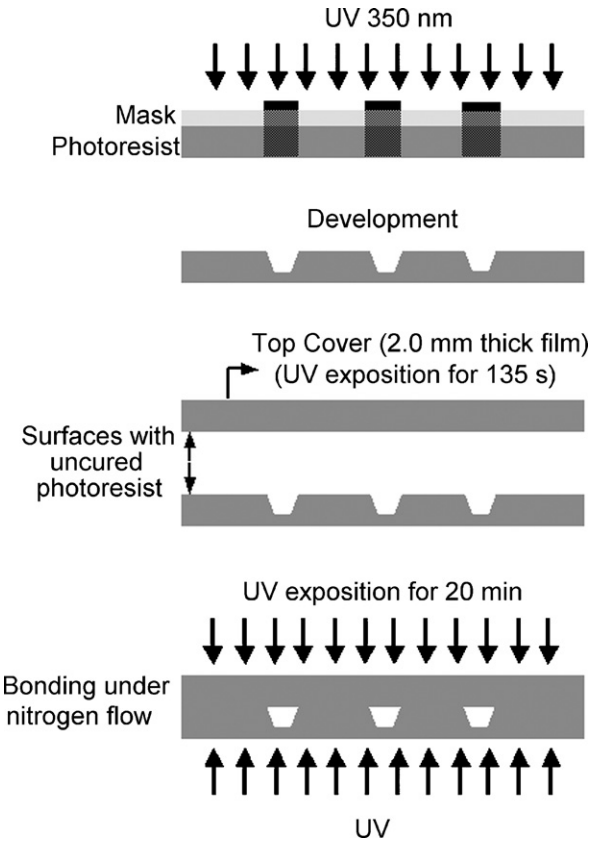

Fig. 2 – Simplified diagram of the whole process for the production of the micro-analyser.

in Fig. 3a. Reference and sample solutions were introduced into the micro-analyser by means of hydrodynamic injection [17] using a sampling plug of 0.30 μL. A Fe(III)/$Hg(SCN)_2$ solution was used as carrier and the flow rate was fixed at 50 μL min^{-1}. Sampling operation, by hydrodynamic injection, was performed with the four solenoid valves (V1–V4) turned on and both pumps (P1 and P2) working in the full-step mode for 25 s. During this procedure, the pumps were run in the aspiration mode, in order to refill P1 with the Fe(III)/$Hg(SCN)_2$ carrier solution, while the sampling loop was filled with the sample solution by means of pump P2. After sampling, all valves were turned off and both pumps started to operate in the reverse direction, in half-step mode, for 50 s. In this way, pump P1 impelled the sample in the reagent carrier solution towards the detector for measurement, while P2 discharged solution to waste, being prepared for the next sampling step. The software was adjusted to acquire 25 absorbance measurements while the sample plug was flowing through the flow cell. A LED, emitting at 470 nm, was used as light source.

To perform the determination of Cr(VI), H_2SO_4 and diphenylcarbazide solutions were propelled at 25 μL min^{-1} by a peristaltic pump (which substituted P1 and P2 pumps), being merged before entering into the micro-system as a carrier stream (50 μL min^{-1}) through V1. Sample plugs of 0.30 μL were introduced into the micro-system by means of hydrodynamic injection, in a similar manner to those described in the determination of chloride. During the sampling step, valve V1 drives the carrier solution to waste, while sample solution is aspirated through valves V2 and V3, filling the sample loop. In the measurement step, all valves were turned off and valve V3 allows the peristaltic pump to aspirate air to waste. Absorbance measurements were performed employing a LED emitting at 525 nm.

3. Results and discussion

3.1. *Characterisation of the micro-system*

After curing the photoresist, a colourless, transparent elastomer was obtained, as shown in Fig. 3b. Fernandes and Ferreira [14] demonstrated that this material does not absorb radiation in the visible range of the spectrum, therefore allowing the use of optical detectors which work in this region of the spectrum. However, the optical fibres themselves were used to seal the detection cell, as even a thin wall of the polymeric material causes light scattering, impairing signal intensity. The connections with the macroscopic world were also successfully implemented. Channels with dimensions slightly smaller than those of the needles and the optical fibres were produced in the micro-system, allowing fitting these objects under pressure. It must be stressed that the couplings of the optical fibres and the needles were made without using any

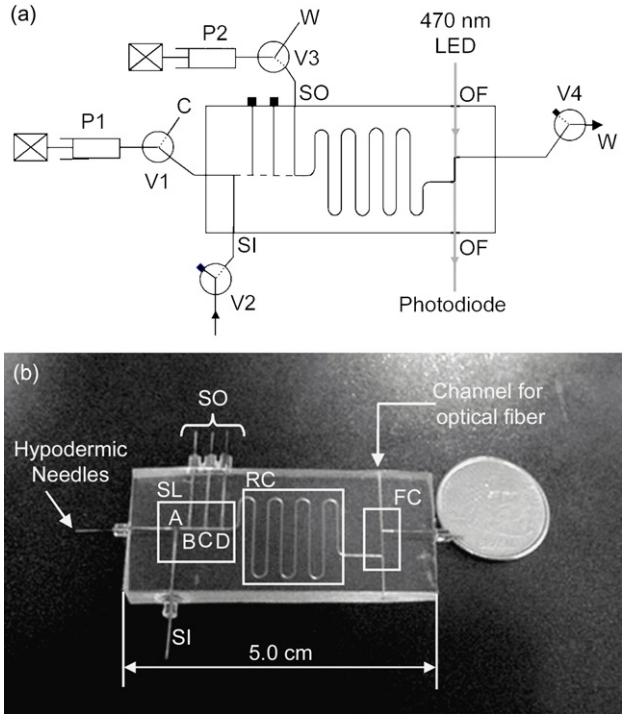

Fig. 3 – (a) Single-line FIA manifold employed for the determination of chloride in waters. P1–P2, piston pumps; V1–V4, mini-solenoid valves (turned off); SI, sample input channel; SO, sample output channels; OF, optical fibre; C, carrier; W, waste. Dashed line shows the sample plug employed for this determination. (b) Photograph of the proposed micro-analyser. SL, sample loops (AB = 0.09 μL, AC = 0.22 μL and AD = 0.30 μL), RC, reaction coil (15 cm), FC, flow cell (5.0 mm pathlength), SI, sample input channel; SO, sample output channels.

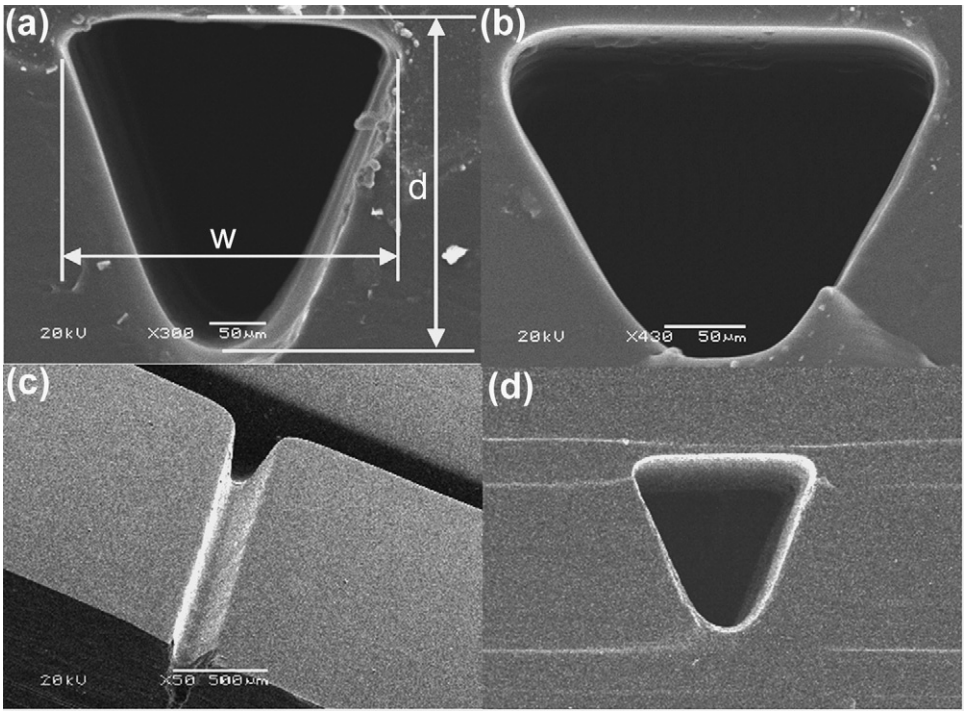

Fig. 4 – Scanning electron micrographs of the channels. (a) Mask lines parallel to the lamps, (b) mask lines perpendicular to the lamps, (c) detail of an open channel and (d) detail of the bonding section.

adhesive, as the polymer has elastomeric properties that allow fitting these objects under pressure. The connections were assessed by passing water through the micro-system at a flow rate of 3.0 mL min^{-1}. No leakage was observed after a period of 30 min, demonstrating the reliability of the connections. In addition, this procedure also confirms the efficiency of the bonding process developed in order to seal the system.

As can be also seen in Fig. 3b, the proposed micro-analyser is as small as a match box (5.0 cm × 2.0 cm × 0.4 cm), holding some of the most common components of a FIA system, such as sample loops (SL), reaction coil (RC, 15 cm) and flow cell (FC, optical path of 5.0 mm). Its design allows performing the basic operations of a photometric determination as in a single line conventional FIA manifold. A volume of 7.0 μL was calculated for the entire system and volumes of 0.09, 0.22 and 0.30 μL were stipulated for the injection loops AB, AC and AD, respectively, based on the dimensions of the channels. The sample volume in the hydrodynamic injection approach is defined by the region between the input channel A and the output channel B–D, which is chosen by the user, before starting the analysis.

Fig. 4 shows some scanning electron micrographs of the channels of the micro-system. It can be seen that channels manufactured by the proposed technique present a triangular cross-section, with dimensions that depend on their relative position in the system. Channels 290 μm wide (w) and

Table 1 – Relationships between the line widths of the mask and the channels dimensions

Mask line width (x) μm	Parallel exposition		Perpendicular exposition	
	Width (w) μm	Depth (d) μm	Width (w) μm	Depth (d) μm
250	197	196	135	95
300	235	225	203	142
350	288	295	265	205
400	347	372	303	271
500	456	483	430	387
600	540	593	527	514
700	648	692	627	612
Relationships	$w = -61.64 + 1.01x$, $R = 0.999$; $d = -98.51 + 1.14x$, $R = 0.998$		$w = -124.95 + 1.09x$, $R = 0.998$; $d = -203 + 1.18x$, $R = 0.999$	

x, line width (in μm) of the mask employed in the CAD project.

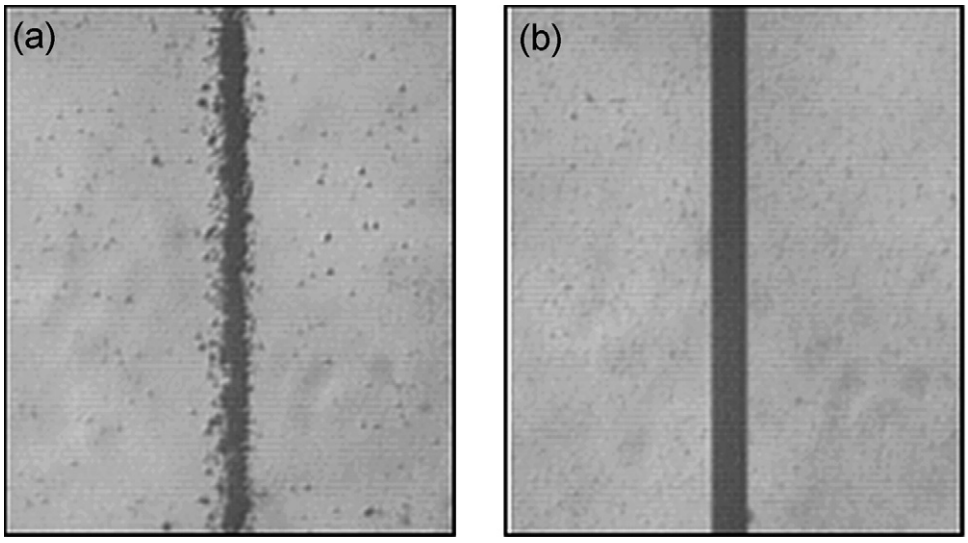

Fig. 5 – Optical micrographs for 100 μm wide lines printed with a (a) laser printer, (b) phototypesetter technology.

295 μm deep (d) were obtained when the line of the photomask was parallel to the lamps of the photoexposer machine (Fig. 4a), while widths of 265 μm and depths of 205 μm were observed for the channels engraved perpendicularly to lamps, as defined by the relative position of the mask (Fig. 4b). The dimensions of the channels were obtained by employing a photomask, whose printed lines were 350 μm wide, indicating that there is a larger penetration of the radiation into the substrate when the perpendicular exposure is used, probably due to light scattering and the use of a non-collimated radiation beam.

Considering the results described above, channels were built on the substrate by using a photomask with lines of seven different widths (250, 300, 350, 400, 500, 600 and 700 μm), in both positions of exposure, in order to evaluate the relationship between the line width of the mask, the position of the light source and the channel dimensions. As shown in Table 1, there is a linear relationship between the line width of the mask and the channel width, which is narrower than the mask line due to the use of a non-collimated radiation beam, as mentioned above. Thus, the equations described in Table 1 can be used to foresee the dimensions of the channels that will be created by the proposed method. However, it is necessary to mention that lines narrower than 200 μm produce channels which are easily clogged during the sealing process, as the mask presents irregularities. As can be seen from the optical micrographs showed in Fig. 5a, the imperfections in toner deposition for a 100-μm line turn the mask inappropriate for use in the photolithographic process. However, this width limit can be surpassed by employing a photomask made by phototypesetter technology, as the quality of the mask produced in this way is enhanced. Fig. 5b shows a mask containing 100-μm line, which produces channels with dimensions of 85 μm (width) and 50 μm (depth) for use in microfluidic systems.

In spite of the mask imperfections, the optical micrograph shown in Fig. 4c demonstrates that the roughness of the channel walls is acceptable for applications in μFIA, while Fig. 4d shows that the top cover layer and the bottom layer containing the channels were successfully bonded using the proposed strategy, which is an improvement of the process recently proposed by Fernandes and Ferreira [14]. This adhesion is effective because a thin layer of uncured photoresist remains on the surfaces of both plates produced in the initial steps of the process, as a consequence of adsorption of oxygen [14] that may act as an intermediary adhesive layer [18] that allows the sealing. When the exposure is made under nitrogen stream, the oxygen is removed, enabling formation of an irreversible adhesion of the two plates. As can be seen in Fig. 4d, there are not imperfections between the two parts, which indicates their good adhesion. It is important to stress that this sealing technique does not demand the use of special equipment or conditions, such as spin-coaters or high temperatures. Therefore, the construction process becomes simpler and cheaper than those usually employed for polymeric devices.

3.2. *Photometric determination*

The FIA microfluidic system was assessed with two different applications, in which the fluids were impelled by a conventional peristaltic pump or a pair of micro-pumps. In both cases, the set of operations necessary to perform a measurement, that is, sampling, injection and acquiring the analytical signal, is similar, as the flow directions are driven by the solenoid valves.

Fig. 6 shows the fiagram obtained in the photometric determination of chloride in waters by employing the micro-analyser, in which the fluids were propelled by the mini-pumps. It can be noted that the fiagram presents a profile similar to those obtained by conventional FIA systems and the baseline exhibits good stability. The precision of the measurements was evaluated by the standard deviations of the peak heights for each set of sample injections with the same concentration, which presented an averaged value of 2.0%. The use of a flow rate of 50 $\mu L\,min^{-1}$ provided an analytical frequency of 45 injections h^{-1}, which is lower than those

Table 2 – Determination of chloride ions in tap and mineral waters

Sample	μFIA[a] ([Cl⁻] mg L⁻¹)	Batch[b] ([Cl⁻] mg L⁻¹)	Deviation (%)
Tap	12.72 ± 0.32	13.37 ± 0.22	−4.4
Perrier	25.24 ± 0.99	26.73 ± 0.38	−5.6
Classic	5.75 ± 0.17	5.53 ± 0.05	+4.0
S. Pellegrino	68.85 ± 1.11	61.62 ± 0.25	+11.7
Lindoya	2.86 ± 0.09	2.97 ± 0.08	−3.7
Schin	17.17 ± 0.35	16.73 ± 0.60	+2.6
Evian	6.65 ± 0.19	6.78 ± 0.18	−1.9
Panna	9.27 ± 0.43	8.76 ± 0.12	+5.8
Serra Negra	1.87 ± 0.14	1.70 ± 0.02	+10.0

[a] Average of four determinations ± standard deviation.
[b] Average of three determinations ± standard deviation. Measurements made in 480 nm with a 1.0-cm pathlength cell.

obtained with a conventional flow manifold (approximately 120 h^{-1}) [19]. Despite this apparent disadvantage, the proposed system produces a residue ca. 0.7 mg of Hg(II) after an 8-h working day (ca. 20 mL of solution), which represents a reduction of approximately 400 times in the generation of residues when compared to an usual FIA system [20]. This fact represents the most important feature of the micro-FIA system, as the reduction of wastes fulfils one of the requirements imposed by Green Chemistry. The analytical curve constructed from the data shown in Fig. 6 showed a good linear relationship ($r^2 = 0.997$), providing a detection limit of 0.96 mg L^{-1}. Table 2 lists the results obtained with the FIA micro-analyser and those obtained with the manual method, which do not show significant differences at a confidence level of 95%.

For the photometric determination of Cr(VI), a peristaltic pump was used to impel the solutions. This kind of pump was chosen in order to demonstrate that the micro-system also works with a standard propelling device, with widespread use in flow analysis. In this case, a relative standard deviation of 1.5% was observed for 10 injections of a solution containing 0.9 mg L^{-1} Cr(VI). The analytical curve showed a linear relationship in the Cr(VI) concentration range from 0.3 to 1.5 mg L^{-1} ($r^2 = 0.999$), with a detection limit of 0.05 mg L^{-1}. The carrier solution flow rate of 50 μL min^{-1} provided an analytical throughput of 80 injections h^{-1}, as the sampling and the reaction times were shorter than those used for the determination of chloride. Table 3 shows the results obtained for the determination of Cr(VI) in underground waters and in Ni–Cr alloys by employing the micro-analyser, which do not present significant differences from those obtained with the manual method at a 95% confidence level.

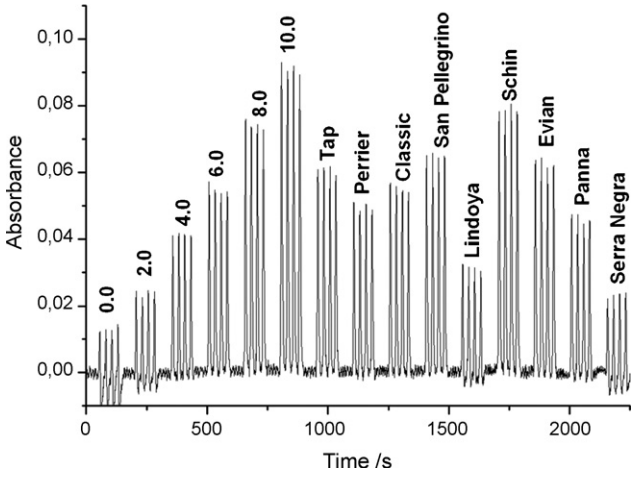

Fig. 6 – Fiagram obtained in the determinations of chloride in tap water and several mineral waters.

Table 3 – Determination of Cr(VI) ions in waters and metallic alloys

Sample	Unit	μFIA[a]	Batch[b]	Deviation (%)
Water A	mg L^{-1}	1034 ± 11	1019	+1.5
Water B	mg L^{-1}	550.0 ± 5.3	512.9	+7.2
Water C	mg L^{-1}	1.33 ± 0.02	1.49	−10.1
Alloy A	mg g^{-1}	100.4 ± 2.2	88.1	+14.0
Alloy B	mg g^{-1}	141.8 ± 2.0	136	+4.3
Alloy C	mg g^{-1}	46.1 ± 0.4	46.8	−1.5

[a] Average of four determinations ± standard deviation.
[b] Measurements made in 525 nm with a 1.0-cm pathlength cell.

4. Conclusions

The micro-flow injection analyser proposed in this work was made with a technique of fabrication which is very simple and easily implemented, avoiding the use of more elaborate methods. A simple and efficient procedure for sealing the micro-system was developed, producing a monolithic system, which can be straightforwardly connected to the macroscopic world and integrated to a photometric detection system, without any leakage under ordinary operation conditions of a flow system. The performance of the micro-analyser in the determination of chloride and Cr(VI) ions permits inferring that it can be a useful device for other applications that also fits the aims of the Green Chemistry.

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