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ORIGINAL ARTICLE

Microchip based sample treatment device interfaced with ICP-MS for the analysis of transition metals from environmental samples

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Abstract A downscaled solid phase (SPE) device applicable for sample preparation prior to ICP-MS monitoring, have been constructed making use of the lab on a chip concept. Standard photolithography and wet chemical etching were used to fabricate glass microfluidic devices accommodating three microchannels, each of them incorporating a defined section that could be packed with SPE materials; selective chelating resin. The microfluidic device was interfaced with the ICP-MS instrument throughout a low flow rate concentric nebuliser using a Teflon connector, and coupled with a flow injection manifold delivering samples and reagents via a manually operated splitting valve. The feasibility of the miniaturized prototype to perform SPE of trace metals was proved by analyzing trace metals, Cd, Co, and Ni, in seawater reference materials; CASS-2 and SLEW-1. The obtained result was in good agreement with the certified values. The device could be used as a remote miniaturized sample treatment for field work.

1. Introduction

Despite the potential advantages associated with on-line sample preparation (Ruzicka and Arndal, 1989; Ruzicka and Hansen, 1975; Olsen et al., 1983; McLaren et al., 1983; Taylor et al., 1996; Kovalev et al., 2000; Zhang et al., 2005; Shariati et al., 2009), there are however indispensable arguments about the cost and sample throughput, especially when instruments with high operating cost such as ICP-MS and ICP-OES are used. This is because the measurement period is only a small fraction of each analysis cycle, during the length of which the instrument is idle waiting for the next sample, thus wasting valuable resource (e.g., argon gas). To make the process cost

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effective, some workers recommended the use of flow injection manifold for sample preparation processing, but instead of on-line analysis, samples are collected in small vessels then introduced to the instrument by conventional means for off-line analysis (Knapp et al., 1987). The process is sometimes called semi on-line SPE (In et al., 1999). Rationally, this procedure is expected to reduce the quantification time and hence save the instrument running cost. However there is a high risk of contamination from equipment and the valuable advantage of analytes enrichment could be lost by the intrinsic dilution. Also, the actual time to complete the whole analytical process might increase.

In recent years, it has been suggested that the applicability of the versatile FIA can be extended to carry out sample preparation in the field simultaneously during sampling, by making use of SPE apparatus (e.g., columns) (Nickson et al., 1999). The technique was originally used to solve problems associated with preserving species during sampling and sample storage in speciation studies of metal ions (Fairman et al., 1995; Blanco et al., 2000). Recently it gained a considerable recognition as a remote sample preparation tool in the field as the portable analytical instrumentation is still far behind the laboratory based instrument in term of selectivity and sensitivity. The approach is well identified nowadays as 'microcolumn field sampling' (MFS) Yebra et al., 2001a,b; Dos Santos et al., 2005. It offers many potential advantages such as, reduction in time and cost spent on sample transportation and storage, and minimisation of loss or change of sample species during transportation and storage. In this technique, samples such as sea water are processed using a simple flow manifold at the sampling site and trace metals of interest are accumulated onto the SPE materials in the microcolumns. The microcolumns are then returned to the central laboratories and again implemented into a FI system for on-line elution and quantification (Fairman et al., 1995; Blanco et al., 2000; Yebra et al., 2001a). Thus, in addition to the previously mentioned potential advantages, the running cost of laboratory based instrument employed for the monitoring and quantification can be significantly reduced because the instrument is required to operate only for a short time during the monitoring period. The principle is also valuable to reduce the cost of elemental analysis process in laboratory based work. However, because this technique makes use of a simple single channel FI manifold incorporating a single column, the replacement of microcolumn with another during quantification requires flow interruption. Therefore, the method's precision and reproducibility would not be ensured. Also the quantification time might be lengthened because of column replacement.

In this work it was proposed that the capability of the microfabrication technology to engineer miniaturised microfluidic devices with a choice of geometrical architectures into small size substrate (Haswell, 1997; Klank, 2003; Rios et al., 2009), can be used to miniaturise a SPE device to the level of lab on chip. The potential advantage of this device lies in the ability to fabricate as many microchannels as needed with exact similarity onto a single microdevice. Once connected to a flow injection manifold either during sample loading or throughout the subsequent desorption and quantification, the flow does not need to be disrupted as with a single column. Thus, in addition to the improved sample throughput, excellent reproducibility can be achieved.

2. Experimental work

2.1. Reagents and chemicals

All reagents used were of analytical grade. High purity water (18 Ω cm resistivity, Elgastat UHQ PS, High Wycombe, UK) was used in solution preparations and super purity nitric acid (Romil, Cambridge, UK) and elemental stock solution (1000 μl ml^{-1}, SpectrosoL, Merck, Poole, Dorset, UK) were used in the preparation of standard solutions. Stock solution (2 M) of ammonium acetate buffer was prepared from the solid and purified by passing through a column of Chelex-100 (BioRad, Hemel Hempstead, UK). The pH was adjusted to the required value with acetic acid or ammonia solution (20% ammonium hydroxide, Romil).

All glasswares were thoroughly cleaned with Lipsol detergent (LIP, Shipley, UK) and soaked overnight in 5% HNO_3. Immediately before use, all acid soaked glassware rinsed with di-ionised water. Reagents and standard solutions were freshly prepared each day before the experiment was carried out.

2.2. Fabrication of glass microfluidic devices

The glass microfluidic devices used in this study were fabricated in house according to a rapid procedure developed by McCreedy (McCredy, 2001) for the microfabrication of glass microchips in the general laboratory. This process uses photolithography to transfer pattern (microchannel network) to the surface of a precoated glass, followed by a wet etching to form the microchannel.

Superwhite Crown B270 glass was obtained precoated with a chromium film and photoresist layer (Photronics, Bridgend, Wales). The required channels network was drawn using a CAD package or CorelDraw. The mask was produced by photo reduction of laser printed drawing onto Kodalith orthofilm type 3 (Kodak professional) at Hull University's photographic services. The mask was then placed over the glass substrate and the channel pattern was photolithographically transferred to the photoresist using radiation using a standard UV exposure unit (Mega Electronics, Linton, Cambridge, UK). The substrate was immersed in a developer solution consisting of 50% microposit developer and 50% deionised water until the pattern was clearly seen, then rinsed with distilled water to expose chromium which was then etched away with chrometch solution. Once the chips had been patterned, they were hard baked for at least 4 h at 120 °C; however, more consistent results are obtained if a minimum of 24 h is employed. After hard baking for sufficient time, the exposed pattern on glass substrate was wet etched using 1% hydrofluoric acid (BDH) buffered with 5% solution of ammonium fluoride at 65 °C for 1 h to engrave the channels pattern. The etched substrate was washed under a running tap until channel were free from deposit and debris and the remaining photoresist could be removed with microposit remover solution and the exposed chrome then removed with chrometch. The clean glass was then washed in detergent solution and dried. This fabrication approach was found to result in channels with good precision.

Thermal bonding was used to bond the top plate of Superwhite Crown B290 borosilicate (Instrument Glass Enfield, UK) incorporating 2 mm predrilled holes, used for tubing connection. In some applications the holes for tubing interface

were drilled at the edge after bonding using a diamond drill. The wafers are cleaned, dried and aligned properly with the aid of a magnifying lens then placed in a furnace. Increasing the temperature slowly to below the glass transition temperature, around 600 °C, was found to result in appropriate bonding if the surfaces are smooth enough and well cleaned. A weight was also placed on the wafers pair to facilitate bonding.

The fabricated microchannels were sealed and packed with chelating resin. The wide sections of channels where SPE materials was packed from the end of the side drilled 1.6 mm i.d. hole, to the beginning of the narrow channel, indicated in Fig. 1 as bold brown lines, was 350 μm wide and 80 μm deep in each channel. The *in situ* miniaturised sample preparation units were created by introducing etchant solution (1% HF/NH_4F) into the closed channels to fill the wide sections. The etchant solution was left in the channels for approximately 10 min and then it was pumped out via the side drilled 1.6 mm i.d. holes. As the etchant was slowly advanced along the channel from channel's inlet, the tapered geometry was created with the tapering occurring in both the width and depth. The process was optimised experimentally to achieve the best packing conditions.

2.3. Microchannel packing

The chelating agent, 8-HQ, immobilised on the CPG (Alsuhaimi, 2007) was dispersed into acetate buffer solution containing 0.01% surfactant (Tween 80, Fulka) to enhance particulates suspension, to form a diluted homogenous slurry. A 5 ml plastic syringe equipped with pieces of 50 μl plastic pipette tip was used to force slurry into the wide channel through the side drilled 1.6 mm i.d. inlets. To prevent small beads from accumulating into the beginning of the tapered channel, which could lead to high pack pressure within the channel or blockage, a tiny amount of large porous CPG beads (CPG-240, 80–120 mesh) was carefully placed at the beginning of the channel to work as a weir (Onuska et al., 1977). It was observed that the quality and density of the packing was improved by applying occasional sonication for short periods of 5 s throughout the packing process. Once the wide sections were homogenously packed to the same length, another minute amount of large beads was placed at the end of the packed large channels, and a 1.6 mm o.d. PTFE tubing, which was used to interface the microdevice with the real world, was inserted in the drilled 1.6 mm i.d. inlets and fixed in place with epoxy glue. The CPG beads could easily be removed by disconnecting the tubing and reversing the process and this meant that if the resin was exhausted, the microdevice could be repacked with new reagent. Flushing the microchannel with a few microlitres of diluted solution of KOH in ethanol was found to be effective in dissolving the CPG beads without any obvious effect on widening the channels. The chip could be repacked as many times as required without the system collapsing. If the microchannels were visibly packed correctly, without gaps or air bubbles, the results obtained from the packed resin were consistent. Sometimes the packing failed, leaving visible channels and gaps and the beads then needed to be removed and repacked. Fig. 2 shows a photograph for a microdevice with the glued connected tubing ready for use.

2.4. Microchip–ICP and FI-microchip interface

The microchip was interfaced to the ICP-MS (Thermoelemental PQ2 +) via a commercially available, low flow rate concentric nebuliser (Micromist, Glass Expansion, Switzerland). This was achieved by using a simple method similar to that previously reported by Song et al. (2003) to interface ICP with microchip for speciation analysis by electrophoresis. Briefly a piece of 30 mm length fused silica capillary (195 μm o.d., 75 μm i.d., Polymicro Technologies, LLC, Ilkley, West York-

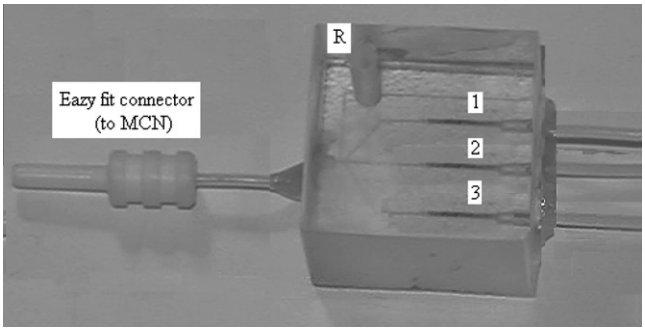

Figure 2 Photograph of the microfluidic device; 1, 2, and 3 indicate the packed microchannels; *R*, make up reservoir. The photo shows the glued connection PTFE tubing to interface the devices with the ICP and the FI manifold.

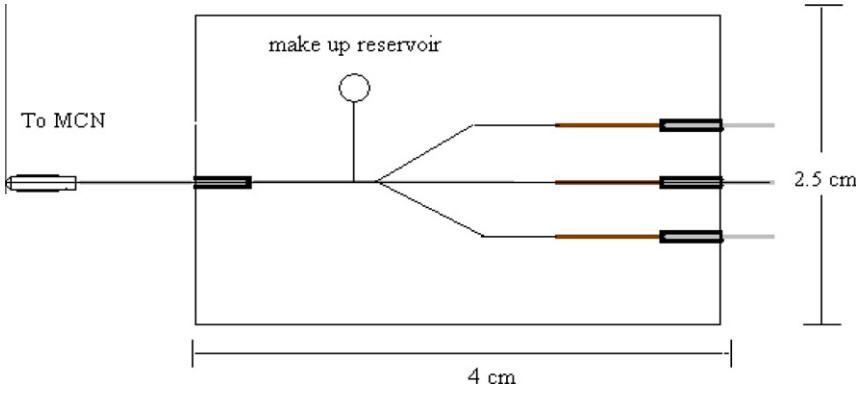

Figure 1 Schematic diagram for the microfluidic device with three packed microchannels (brown lines) and the glued connection PTFE tubing for its coupling with FI and the interface with ICP-MS.

shire, UK) supported by being encapsulated inside a PTFE tube (1.6 mm o.d., 200 μm i.d., VWR International Ltd., Lutterworth, UK), was inserted into the 1.6 mm i.d. drilled hole at the exit port of the channel and held in place with a thin layer of epoxy glue (UHU plus, Germany). The other end was then directly connected to the nebuliser by using a Teflon connector (EzyFit, Glass Expansion, Switzerland) as shown in Fig. 3. A miniature jacketed (4 °C) cyclonic spray chamber (Cinnabar, Glass Expansion, Switzerland) was used to obtain high sample introduction efficiency with the low flow rate.

The manipulation of solutions (i.e., on-line buffering, sample loading and elution) in this study was performed using simple flow injection manifolds constituted of a four channel Gilson Minipuls-3 peristaltic pump (Gilson, Inc., Middleton, USA) fitted with PVC pump tubing, PTFE transportation tubing (0.3 mm i.d., 1.6 mm o.d., Omnifit) and 4-way selection valves (Omnifit). To match the low flow rate allowed by the microchannels, a restriction valve was implemented in the manifold immediately behind the microchip connection junctions. Once this valve was partially open, the main stream could be split in controllable ratios with excellent precision. To minimise the dead volumes within the connection fitting, the FI-microchip interface (tubing from the microchip to the valves) was constructed from 40 mm length fused silica capillary (195 μm o.d., 75 μm i.d.) supported by being inserted inside a PTFE tube (1.6 mm o.d., 200 μm i.d.). One end of each PTFE tube was inserted into the drilled hole and fixed in place with epoxy glue while the other end was furnished with a standard screw fitting and connected to the main stream via three 3-way '*T*' valves (Omnifit, UK). Thus the microchip could be simply replaced with another with minimum connection fitting points.

The lowest stable uptake flow rate of the utilised nebuliser was about 42.5 μl min^{-1} whereas the flow rate through the packed channels was controlled by the splitting valve and the peristaltic pump (Minipuls-3, Gilson) to give an appropriate flow rate in the range 10–20 μl min^{-1}. The makeup solution was delivered by peristaltic pump to the makeup reservoir. These manifolds are schematically presented in Fig. 4.

2.5. Analytical procedure

The microfluidic device was implemented into the FI system (as in Fig. 4) and a solution of 1.0 M HNO_3 was propelled throughout the system to flush any residual trace metals within the connection tubing or the microchannels for at least one hour. Afterward, the system was cleaned by running deionised distilled water through for 30 min. Once the whole system was cleaned, sample or standard was buffered on-line and loaded through the packed microchannels at a flow rate of 20 ± 2 μl min^{-1} for therequired periods, then the selection valve was switched to allow water to wash the microchannels to strip off any residual non retained metals within packed microchannels or the connection tubing. The loaded microdevice was then transferred to the ICP-MS laboratory where it was incorporated into another FI manifold interfaced with ICP-MS. Once it was incorporated into the elution manifold, and a stable signal from internal standard solution (50 ng ml^{-1}) in the make up reservoir was obtained, the selection valve was switched to the 1.0 M HNO_3 position to elute the sorbed trace metals from the packed microchannels sequentially into the ICP-MS for monitoring and quantification. TRA software from Thermo Elemental was used for off-line data processing. The operating conditions during elemental analysis for ICP-MS were as in Table 1.

3. Results and discussion

3.1. Initial development of the microchip with packed channels

In this work it was proposed that sample preparation systems relying on the use of SPE equipments (e.g., columns) can benefit from the new development in miniaturisation technology based on lab a chip concept. In this context, the potential of microfabrication techniques like lithography and chemical etching to construct many identical features on a single glass microchip, with excellent precision, could be utilised to fabricate microchip incorporating many integrated SPE apparatus. This will make it possible to replace the conventional systems based on single column, with a single miniaturised microfluidic device incorporating SPE segments within the etched microchannels. Therefore, besides the potential advantageous that can be accomplished from device miniaturisation, multiple and parallel processing could be easily achieved.

Initially, many attempts were made to craft a short section of porous monolithic silica inside a single microchannel fabricated within a glass microfluidic device using sol gel process as described elsewhere (Alsuhaimi, 2007). However, these efforts did not succeeded because it was not possible to localise the silicate solution to polymerise at the desired location within a confined short section. To alleviate this limitation it was proposed to attach the chelating reagents onto the inner surface of microchannels. Even though this method was easily practiced and permitted a successful immobilisation, it was restricted by the insufficient surface area, as the preliminarily

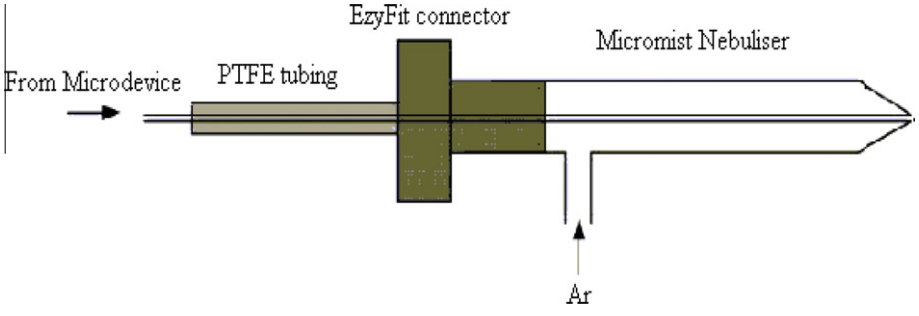

Figure 3 Schematic diagram of microchip–ICP interface (Song et al., 2003).

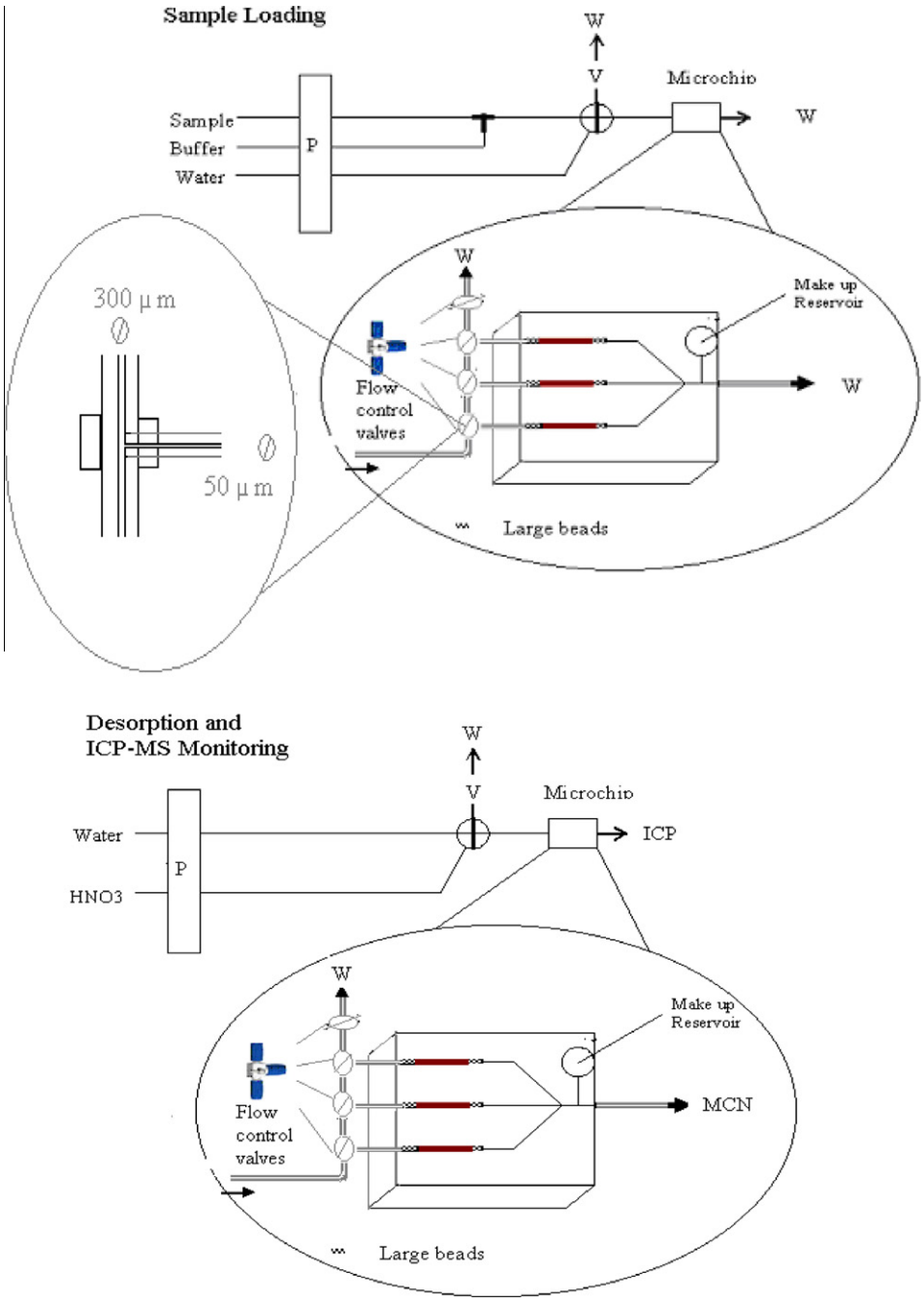

Figure 4 Flow injection manifolds for trace metals sample loading, and desorption and monitoring. P, peristaltic pump; V, flow selection valve; W, waste; MCN, micro-concentric nebuliser; V, flow selection valve; ICP, inductively coupled plasma.

results proved that the enriched ions on the chelating reagents immobilised on the inner surface of a 30 mm length microchannel could not be quantified using the best excellent available detector (i.e., close to the detection limit of ICP-MS for many metals). Therefore, it was suggested that increasing the surface area by generating a thin layer of porous silica could resolve this dilemma. This was undertaken making use of a short capillary (50 mm length and 0.3 mm i.d.) following a reported method designed to generate a layer of silica whiskers on the inner wall of glass capillary for open capillary chromatography (Banu et al., 2003). In this process, a solution of ammonium hydrogen fluoride is allowed to flow through glass capillary at a very low flow rate ($\approx$10 µl min^{-1}) for about 4 h in order to etch the surface. The dissolved silica in the etching process may redeposit on the inner surface because the hydrodynamic flow is not sufficient to flush it away. A baking step at 400 °C in an oven for about 8 h is subsequently applied to affix the deposited silica layer to the capillary wall. The successfulness of this method was evidenced from the appearance of a thin layer of white silica material on the inner wall of the capillary. The deposited porous material covering the capillary inner surface was functionalised with 8-hydroxyquinoline

Table 1 The operating condition of ICP-MS system during the analysis.

Forward power/W	1350
Reflected power/W	1–3
Cool gas/l^{-1} min	14
Auxiliary gas/l^{-1} min	1.2
Nebulising gas/l^{-1} min	0.890
Spray chamber	Glass, water cooled at 4 °C
Data acquisition mode	Peak jumping
Point per peak	3
Dwell time	10.24 ms
Detection mode	Pulse counting
Isotopes	^{111}Cd, ^{59}Co, and ^{60}Ni,
Internal standard	In

following the immobilisation protocol previously described for monolithic silica. This coated silica capillary, however, exhibited good stability in aqueous buffered solution or organic solvent during the immobilisation process but dislodged from the capillary with acidic solutions during metals' desorption. This phenomenon may be due to the effect of acidic solution on breaking the bounding attaching the deposited silica to capillary surface. Thus, this approach was considered to be impractical for on chip applications and was not investigated further.

As both of the previous attempts failed to produce adequate solid support within the channels or capillaries, the packed channel was considered to be a good alternative. Thus, glass microchips incorporating three microchannels were fabricated by means of lithography and wet chemical etching as in Section 2. Within each individual microchannel, a small section that could be packed with SPE materials such as immobilised bead was fabricated. Initially, a single channel was fabricated in a glass microchip device using a design developed for an immobilised enzyme packed bioreactor (Banu et al., 2003). However, the process of packing the glass microchip was not straightforward; frequently, larger beads accumulated in the side channel and the corners, and therefore blocked the microchannel. Unlike glass microchips with PDMS cover which can be removed and cleaned and packed again, the blockage of glass microchannel covered with a glass top can be a terminal problem. Therefore, a simple straight channel was suggested to be more practical as bead slurry could be injected more easily into the straight channel than pushed from a side channel then sucked into the packed section (Banu et al., 2003). The straight channel design is more useful in fabricating microfluidic devices with multi channel facility as many identical channels can be etched in small substrate. Once packed and interfaced properly with the system for fluidic handling, this device will be a useful miniaturised means of sample preparation in the analysis of trace elements.

In this work the feasibility of fabricated miniaturised devices to operate as remote systems was demonstrated by carrying out sample preparation and the subsequent monitoring in different locations and at different times to resemble field work. In other words, sampling and sample preparation were undertaken at the research laboratory and then the microdevices either taken to the ICP laboratory for quantification or stored in the cold room for later analysis. This was confirmed further by stability study (as will be described bellow).

3.2. Interfacing the microfluidic device with real world and ICP-MS

The microdevice was interfaced with a simple FIA system for solution manipulation. Thus the washing, conditioning, and sample loading through packed channels could be accomplished simply by directing the flow through them sequentially by means of 3-way valves. The low flow rate in the µl min^{-1} range required for sample manipulation within micro fluidic devices was achieved using the flow splitting principle. This was made possible by using a two way valve on the main stream but close to the micro devices. The valve can be used (partially opened or closed) to establish a stable splitting ratio up to 1:10 for the original main stream. All transporting lines constructing the FIA manifold were made from PTFE tubing of 170 µm i.d. to minimise the dead volume within the manifold or in the connection points. Also the use of small diameter tubing would be useful in order to sustain minuscule flow rates compatible with miniaturised microdevices, either directly or throughout simple splitting tools.

The long term stability of the flow rate was studied at 21 ± 2 µl min^{-1} through the microchannel for 16 h; the results were shown in Fig. 5. The original stream propelled by peristaltic pump at 80 µl min^{-1} was split up by proper adjustment of the controlling valve. Although it is possible to use higher flow rate with packed microchannels, ca. 100 µl min^{-1} (Banu et al., 2003), the flow rate (21 ± 2 µl min^{-1}) was chosen to avoid progressive tightening of the packed beads in the narrow ends of the tapered microchannels, which could influence flow stability.

The feasibility of packed microchannels to function as miniaturised SPE apparatus for transition metal ions was studied by the use of three metal ions, Cd, Co, and Ni, as illustrative examples. These metal ions were chosen because of their low blank. The SPE studies were conducted with standard solutions containing 5 ng ml^{-1} of each ion. The standard was buffered on-line as in Section 2, and loaded for abut 90 s. The channels were then washed with buffer and water, and subsequently the microdevice was transferred to the ICP laboratory where it was implemented into an FI manifold coupled with ICP-MS for on-line elution and monitoring. A typical elution profile is shown in Fig. 6. The elution peaks are depicted by the ICP-MS counts response vs. time. The peaks have basic Gaussian shapes with slight tailing. The half width of elution peaks for the studied metals are 1.8, 2.3, and 2.7 s, which are equivalent to 63, 80.5, and 98 nl for Cd, Co, and Ni,

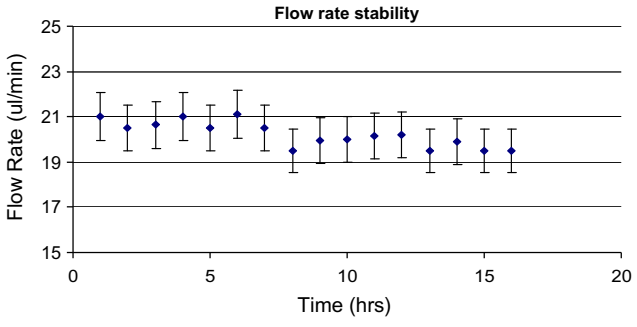

Figure 5 Flow rate stability at 20 µl min^{-1} maintained by splitting the main stream using a controlling valve.

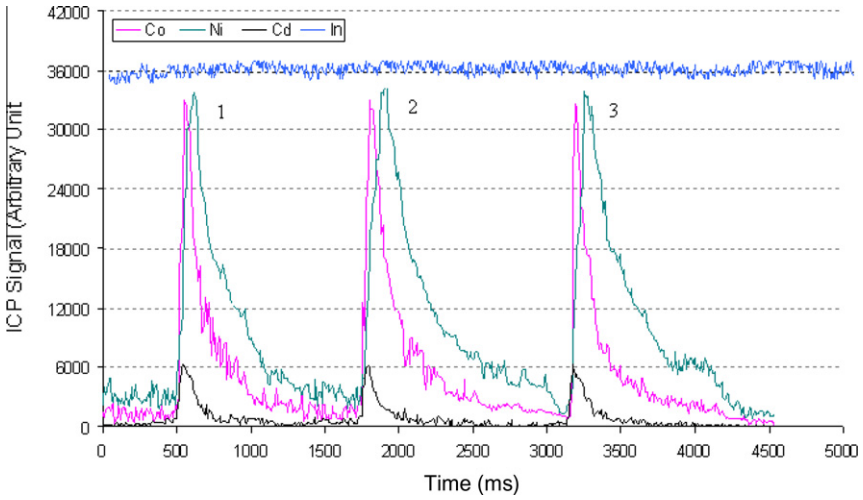

Figure 6 Multielement scans showing the elution profiles for studied metals in standard solutions containing 5 ng ml^{-1} loaded for 90 s. Also shown is the stable baseline signal from 50 ng ml^{-1} internal standard, In.

respectively. The figure also shows an interesting similarity among the peaks related to the same metal eluted from three identical microchannels. At the tested concentration, 5 ng ml^{-1}, between-channel relative standard deviations for Cd, Co, and Ni were 4.7%, 6.4%, and 6.8% in that order.

3.3. Breakthrough of packed microchannel

The breakthrough values of the packed channels for the studied elements were investigated. The test was performed using a single channel as they are identical. A standard solutions containing 20 ng ml^{-1} of each metal individually loaded for different periods of time at fixed flow rate i.e., 20 µl min^{-1}. As can be seen in Fig. 7, the ICP-MS signals for each metal increases linearly with increased loading time for all metal ions, before reaching a plateau around 120 s. This is a useful procedure to estimate the saturation values for the packed microchannels, since it is not easy to measure the mass of the packed resin precisely. In addition, it gives an essential idea about the possible dynamic range in which these miniaturised devices can be applied.

3.4. Calibration and analysis of CRMs

The feasibility of the constructed microdevice to function as an efficient sample preparation (eliminate matrices) devices, was examined by analysing selected trace metal ions in seawater. Calibration curves of four points across the concentration range of 0–0.5 ng ml^{-1} for Cd and Co, and 0.1–1.0 ng ml^{-1}

Table 2 Calibration data for packed microchannels.

	Cd	Co	Ni
RSD at 0.25 ng ml^{-1} (%n = 3)	2.47	2.09	3.03
Calibration coefficient R^2	0.997	0.999	0.996
LOD/ng ml^{-1}	0.008	0.006	0.009

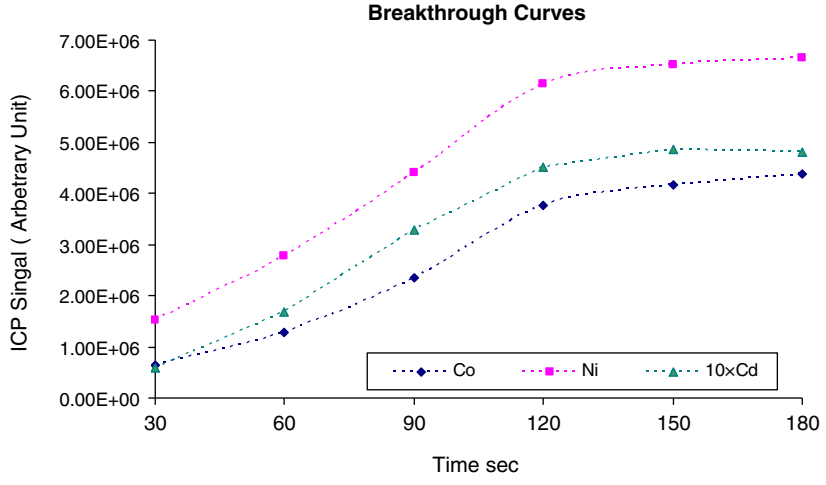

Figure 7 Breakthrough of the packed microchannel obtained using standard solutions of 20 ng ml^{-1} of Cd, Co, and Ni loaded at 20 µl min^{-1}.

Table 3 Analysis results for reference materials CASS-2 and SLEW-1. Concentration in ng ml^{-1} (at 95% confident limit, $n = 3$).

Metal	CASS-2		SLEW-1	
	Measured (recovery%)	Certified	Measured (recovery%)	Certified
Cd	0.021 ± 0.003 (110%)	0.019 ± 0.004	0.020 ± 0.004 (111%)	0.018 ± 0.003
Co	0.025 ± 0.008 (100%)	0.025 ± 0.006	0.045 ± 0.006 (97.8%)	0.046 ± 0.007
Ni	0.297 ± 0.043 (99%)	0.2987 ± 0.036	0.749 ± 0.026 (100.8%)	0.743 ± 0.078

for Ni, were generated. The calibrations were obtained by loading a series of standards prepared in acidified pure water (0.1% nitric acid), using the flow manifold, where samples are buffered on-line prior to passing through the microchannels. Then the loaded standard was eluted to the ICP-MS for quantification. The applicability of calibrations curves obtained from standards to compute ions' concentration in seawater was confirmed in previous studies by Greenway and co-workers. Their investigations proved that simple pure water calibration solutions can be used to determine analytes in more complex matrices. (Nelms et al., 1995; Greenway et al., 1996) The calibration parameters obtained from acidified standards are presented in Table 2.

Real samples CASS-2 and SLEW-1 were treated in a similar way. The determined values alongside with the certified values are tabulated in Table 3. As can be seen in this table, the measured concentration using this method agrees with the certified values. Apparently, the measured values for Cd in the two samples are bellow the quantification limit (calculated based on LOQ = 3.33 × LOD). This may explains the high recovery values (which may result from the uncertainty associated with the quantification). However, the overall results prove the feasibility of this device as an efficient miniaturised sample preparation tool.

3.5. Stability of the microdevice

One of the proposed applications of these microchips is to be utilised for temporary sample storage. Therefore a stability study was conducted to investigate this feasibility. In this assessment, standard solutions containing 5 ng ml^{-1} of the studied ions were loaded into the packed channels, and then the microchips were stored in the fridge at 4 °C for up to 7 days. As can be seen in Fig. 8, all metal ions were recovered quantitatively in the first four days; afterward the recovered amounts started to decline steadily to values below 50% after 7 days. Similar findings, however, have been reported by other worker for the packed minicolumns (Kovalev et al., 2000). The diminution in the recovery as a function of storing time may be ascribed to the leaching out of the retained ions with water remaining in the PTFE tubes connected to the devices or might be due to beads drying during storing for an extended period because the low amount of water within the dead volume. However, this miniaturised device offers potential advantages to be used as an efficient tool to perform sampling and sample preparation simultaneously (could be in the field) and for temporary storage i.e., it is not necessary to take and/or process the samples and analyse them within the shortest possible time. Furthermore, as sample manipulation steps are minimised using these devices, they would be attractive tools in speciation studies to obtain a truer representation of the actual species in the original samples than with conventionally taken samples, which are subject to possible pH and temperature changes before analysis. In this respect, the use of highly selective reagents that could bond certain species is much preferred. For instance, the recently reported silica-immobilised purpurolgallin (Mahamoud and AlSaadi, 2001), which showed high selectivity for Fe(III) in presence of other ions, can be employed as packing materials in the miniaturised devices to preserve Fe(III) from water samples.

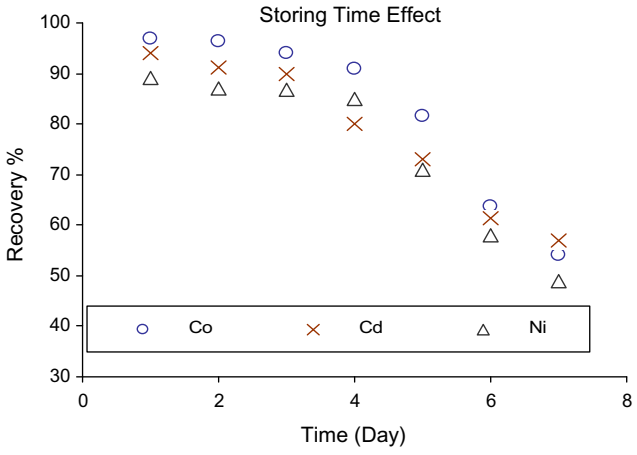

Figure 8 Effect of storing time on metals recovery.

4. Conclusion

The work in this article demonstrates a microfabrication process based on lab on chip technology to construct miniaturised microfluidic devices incorporating multi channels having the status of sample preparation tools. Glass microchip containing three etched microchannels, each of which incorporates a short section packed with resin, which can function as an integrated sample preparation for trace metals, was fabricated using lithography and wet etching. A technical approach to interface these devices with the real world e.g., FI system executing sample and reagents manipulation, and to effect its coupling with an ICP-MS instrument, has been described. The system demonstrated excellent performance as a miniaturised sample preparation apparatus for trace elements in seawater (i.e. Co, Cd, and Ni) prior to ICP-MS monitoring. The developed procedure has been validated using seawater standard reference materials in laboratory, however, the device is ideal for simultaneous sampling and sample preparation in field based work.

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