Spectrochimica Acta Part B 126 (2016) 23–30

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

The feasibility of liquid sample microanalysis using polydimethylsiloxane microfluidic chips with in-channel and in-port laser-induced breakdown spectroscopy detection

Anikó Metzinger [a], Andrea Nagy [b], Attila Gáspár [b], Zsuzsanna Márton [c], Éva Kovács-Széles [d], Gábor Galbács [a,*]

[a] Department of Inorganic and Analytical Chemistry, University of Szeged, 6720 Szeged, Hungary
[b] Department of Inorganic and Analytical Chemistry, University of Debrecen, 4010 Debrecen, Hungary
[c] MTA-PTE High-Field Terahertz Research Group, Institute of Physics, University of Pécs, 7624 Pécs, Hungary
[d] Nuclear Security Department, Centre for Energy Research, Hungarian Academy of Sciences, 1121 Budapest, Konkoly-Thege Miklós way 29-33, Hungary

ARTICLE INFO

Article history:
Received 30 May 2016
Received in revised form 4 October 2016
Accepted 17 October 2016
Available online 18 October 2016

Keywords:
Laser-induced breakdown spectroscopy (LIBS)
Lab-on-a-chip (LOC)
Polydimethylsiloxane (PDMS)
Microfluidics
Laser ablation
Chromium

ABSTRACT

This study describes the direct interfacing of polydimethylsiloxane (PDMS) microfluidic chips with laser-induced breakdown spectroscopy (LIBS) detection. The changes induced in the PDMS material by nanosecond laser ablation are briefly documented by using optical microscopy and scanning profilometry. The main part of the study focuses on the solution of technical and analytical problems of coupling single-pulse LIBS detection with PDMS microfluidic chips in order to assess the feasibility and performance of the concept of creating a lab-on-a-chip device with LIBS detection (LOC-LIBS). Multiple optical and sample presentation schemes including in-channel and in-port detection were tested, but it was found that LOC-LIBS is only viable and practical with in-port detection outside the chip. It was shown that LOC-LIBS in this configuration is capable of the trace speciation analysis of chromium using as little as 0.5 μL solution volume. The achieved absolute limit of detection was 2 ng.

1. Introduction

Micro total analytical systems (μ-TAS) or lab-on-a-chip (LOC) devices are attractive because their use can be largely automated and they offer a microfluidic platform for the sample preparation and/or analysis of liquid samples, requiring low sample and reagent volumes (e.g. in the nL to μL range). The short liquid pathways promise fast analyses, and the closed channels even provide a safe way for the analysis of biologically or chemically hazardous materials - especially if the channels are made of some cheap material (e.g. polymer) so that the chip can be disposed after use. Disposable chips can also make complex, but important analytical procedures (e.g. medical screening) available in places where running a full chemical lab is not feasible [1,2].

At present, one of the most often used technical polymer for LOC systems is polydimethylsiloxane (PDMS). It is a soft elastomer with excellent physical and chemical properties, such as curing at low temperatures, inertness, controllable surface chemistry, low permeability to water, non-toxicity and non-flammability, insolubility in water and alcohols, etc. It is also optically transparent down to 240 nm and a good electrical and thermal insulator [3,4]. Completed PDMS devices can be easily interfaced with silica or polymer layers. Fabrication methods most often employed with PDMS include replica molding, soft lithography and rapid prototyping [5,6].

Most LOC systems are made for liquid sample preparation (chromatographic and electroforetic lab-on-a-chip systems are most popular) with the detection typically left to off-chip, laboratory instruments [1,2,7,8]. Among the detectors actually used on-chip are some electrochemical sensors [9–13], and certain optical detection schemes, such as UV–Vis absorption or laser induced fluorescence spectroscopy using fiber-optics based light guiding and semiconductor laser-based excitation [14–17]. Most recently, even atomic spectroscopy detection, which is complicated by the requirement of generating a high temperature atom source, has also been successfully miniaturized. Several mm-sized microplasma devices (e.g. dielectric barrier discharges, microwave plasmas) have been reported to work under conditions that may be compatible with LOC operation [18,19].

Laser-induced breakdown spectroscopy (LIBS) is a versatile, powerful and robust atomic emission spectroscopy technique. It's operation is based on focusing a high-power, pulsed laser beam onto/into the sample, in order to ablate the sample and generate a plasma (laser-induced breakdown plasma, or LIB plasma for short). By the collection and evaluation of the emission spectrum of this plasma, both qualitative and quantitative analytical data can be acquired about the sample. LIBS is quite popular these years; in fact, the majority of new publications within the field of atomic spectroscopy is nowadays produced by LIBS research [20]. The popularity of LIBS is due to the fact that it offers a

* Corresponding author.
E-mail address: galbx@chem.u-szeged.hu (G. Galbács).

http://dx.doi.org/10.1016/j.sab.2016.10.014
0584-8547/

unique set of advantageous analytical and technical characteristics. It is a versatile, non-contact method, which is capable of providing elemental composition data (either at the level of trace, minor or major components) for practically any samples (solids, liquids or gases), in a virtually non-destructive way, without any significant sample preparation, thus the analysis is very fast too. The instrumentation needed is reasonably simple, very robust, and is also available in such a compact format, that it allows portable operation or even space applications [20–23].

Direct liquid sample analysis by LIBS is still a challenging application [20,24], which is hampered by focusing and light collection problems associated with the mobile free liquid surface and bubble formation, etc. In addition, the plasma formation in liquids (e.g. water) is significantly suppressed by the incompressibility and high thermal conductance of liquids, which result in poor emission signals. Nevertheless, these problems can be overcome by using special sample presentation techniques such as sample introduction via nebulization [25,26] or liquid jets [27], as well as by liquid-to-solid conversion [28–30], or by using the double-pulse LIBS approach [24,31].

The combination of LOC with LIBS detection (LOC-LIBS) has a great analytical potential, especially for liquid sample analysis. On one hand, microfluidic chips are low-cost, very practical devices for low-volume, semi-automated, closed-system liquid sample preparation. On the other hand, LIBS instrumentation can be made compact and relatively low-cost, which requires very small sample volumes and can provide direct analysis of the elemental or isotopic components of liquid samples. Interfacing LIBS to optically transparent polymer chips can be assumed to be relatively easy, e.g. by using fiber-optics light guiding for both the excitation and light collection.

In the light of the above, it is interesting that so far only in a single study, to the knowledge of the authors of the present work, has been the combined use of microfludics and LIBS suggested and tested [32]. The Fedosejevs group demonstrated the feasibility of building a microfludics-based nano droplet sample introduction device (a thermally actuated micro-nozzle nebulizer) for LIBS sample introduction. A patterned thin film resistive element super-heated the liquid sample flowing in a channel in tens of microseconds time and created a micro-bubble that extruded a hemispherical, 6 pL volume micro-droplet from the microchip. Sodium was successfully detected by LIBS in this microdroplet achieving 60 ppm limit of detection. Yet, this device was not a lab-on-a-chip device in the fullest sense, as no additional analytical function (e.g. sample pretreatment, separation, enrichment, etc.) was added to the microfludic channel.

Involving sample preparation in the process of LIBS analysis might seem, at the first glimpse, to be a notion that makes no sense, as this concept would eliminate one of the most esteemed features of the technique, namely that it requires very little if any sample preparation. In reality however, this concept makes perfect sense. For example, direct liquid sample analysis is the LIBS application field which de facto requires some sample preparation, as it has been alluded to above. In addition, the sample preparation can enable the use of well-established analytical approaches, such as sample buffering, enrichment, standard addition, etc. In fact, most recently researchers have started to explore the feasibility of adapting conventional macro-scale liquid sample preparation methods, such as preconcentration or extraction, to micro-volume liquid samples prior to their LIBS analysis. For example, single-drop microextraction (SDME) [33] and dispersive liquid-liquid microextraction (DLLME) [34,35] of chelated metal ions were carried out. Other groups reported about successful preconcentrations carried out by the electrodeposition of metal ions [36], or by using ion-exchange polymer membranes [37].

The laser ablation of polymer layers in atomic spectrometry is an upcoming methodology. This serves, for example, the purposes of bioimaging by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), where soft biological samples are encased in a hard polymer matrix (e.g. epoxy resins) to facilitate microtome slicing [38,39]. Few other related applications perform the LIBS [40] or LA-ICP-MS [41,42] analysis of gel electrophoresis spots for elemental speciation.

The aim of the present study was to assess the feasibility of the direct coupling of PDMS microfluidic chips to a LIBS detector for liquid sample trace analysis. In this combination, the microchip can provide small-volume sample preparation, whereas LIBS can offer element selective detection capabilities. The detailed assessment of this analytically appealing concept includes the study of the behaviour of PDMS polymer under the influence of laser ablation, the evaluation of various potential options for the LOC-LIBS interfacing, and finally the testing of the analytical capabilities of the system in a Cr(III)/Cr(VI) speciation application.

2. Experimental

2.1. Preparation of microfluidic chips

PDMS chips in this study were created by using soft photolitography [43,44]. The microfluidic pattern was designed in AutoCAD (AutoDesk, USA) software and turned into a photomask by printing it with a 3600 dpi resolution onto a transparency film. This photomask was then used in 1:1 contact photolithography using a photoresist (SU-8, Microchem, USA), spin-coated onto a pre-cleaned 3″ silicon wafer, and irradiation with 365 nm UV light. This master consisted of a positive relief and served as a mold for PDMS in a Petri dish. The flexible PDMS polymer was prepared by using the Sylgard 184 commercial kit from Dow Corning (USA), that contains a 10:1 mixture of PDMS oligomer and cross-linking agent. Stirring and degassing under vacuum was used to remove any gas bubbles that may have formed during polymerization. The pre-polymer was poured onto the master to form a ca. 3 mm thick layer, and was cured for 60 min at 65 °C. The PDMS replica was then peeled off from the master, the ports were created by a hole puncher and the PDMS surface was cleaned with methanol and then sealed using plasma oxidation to either another flat layer of PDMS, or a flat glass or quartz plate (standard size microscope slides) to form the microfluidic channels.

Some glass and quartz microscope slides used for the preparation of the chips contained fabricated “pockets” (pits) that served as effluent containers. The diameter of these pockets was 1 mm, and they were machined using a computer numerical control (CNC) engine. After machining, the slides were thoroughly cleaned with “Piranha” solution (a 3:1 mixture of trace analytical purity cc. H_2SO_4 and 30% H_2O_2).

2.2. Instrumentation

Two laser systems were employed during the experiments. In laser ablation experiments, we used a Thunder Art Nd:YAG laser (Quanta Systems, Italy), capable of emitting single laser pulses at the fundamental, second and fourth harmonic wavelengths (1064, 532 and 266 nm) with maximum useful pulse energies of 900, 500 and 220 mJ, respectively (Laser system A). In this study, only the fundamental wavelength output from this laser was used. The pulses were 7–9 ns in duration and could be generated with a maximum repetition rate of 20 Hz. The laser beam was focused on the sample surface with a 50 mm focal length, fused silica plano convex lens (the beam was f/3) and the focal spot had a slightly elliptical cross section with ca. 200 × 350 μm axial sizes. The laser was operated with 90, 150 and 210 mJ pulse energies corresponding to a fluence range of 160 to 382 J/cm^2.

The laser used in analytical LOC-LIBS experiments was a passively Q-switched LIBScan 25 + laser from Applied Photonics, UK (Laser system B). This laser is able to emit single pulses at 1064 nm with a pulse energy of 50 mJ. The laser pulse duration is 4 ns. The focused beam in the focal spot was slightly elliptical with ca. 200 × 300 μm axial sizes. The beam was f/3 and the fluence used was about 100 J/cm^2. All LIBS spectra were recorded using an AvaSpec-FT2048 fiber optic CCD spectrometer (Avantes, NL) in the 198–318 nm UV and 344–888 nm Vis spectral ranges with optical resolutions of 0.09 and 0.4 nm, respectively. Light