



Contents lists available at ScienceDirect

Analytica Chimica Acta

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

A high-throughput solid-phase extraction microchip combined with inductively coupled plasma-mass spectrometry for rapid determination of trace heavy metals in natural water



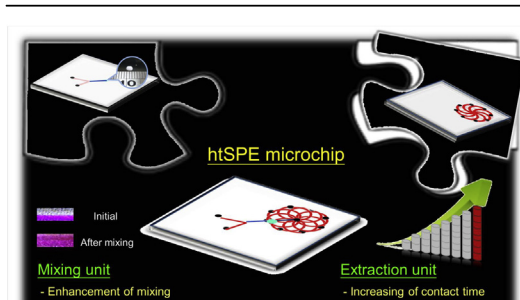
Tsung-Ting Shih, Cheng-Chuan Hsieh, Yu-Ting Luo, Yi-An Su, Ping-Hung Chen, Yu-Chen Chuang, Yuh-Chang Sun*

Department of Biomedical Engineering and Environmental Sciences, National Tsing Hua University, 30013, Hsinchu, Taiwan

HIGHLIGHTS

- An htSPE microchip–ICP–MS system was developed for trace metal analysis.
- An htSPE microchip consisted of a micromixer and a multi-channelled extraction unit.
- Detection limits of 1.64–42.54 ng L⁻¹ for the metal ions were achieved.
- Each analysis could be readily accomplished within just 186 s.
- This method was successfully used for the analysis of metal ions in natural water.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 September 2015

Received in revised form

20 January 2016

Accepted 22 February 2016

Available online 24 February 2016

Keywords:

High-throughput solid phase extraction

Inductively coupled plasma-mass

spectrometry

Micromixer

Multi-channelled

Automation

ABSTRACT

Herein, a hyphenated system combining a high-throughput solid-phase extraction (htSPE) microchip with inductively coupled plasma-mass spectrometry (ICP-MS) for rapid determination of trace heavy metals was developed. Rather than performing multiple analyses in parallel for the enhancement of analytical throughput, we improved the processing speed for individual samples by increasing the operation flow rate during SPE procedures. To this end, an innovative device combining a micromixer and a multi-channelled extraction unit was designed. Furthermore, a programmable valve manifold was used to interface the developed microchip and ICP-MS instrumentation in order to fully automate the system, leading to a dramatic reduction in operation time and human error. Under the optimized operation conditions for the established system, detection limits of 1.64–42.54 ng L⁻¹ for the analyte ions were achieved. Validation procedures demonstrated that the developed method could be satisfactorily applied to the determination of trace heavy metals in natural water. Each analysis could be readily accomplished within just 186 s using the established system. This represents, to the best of our knowledge, an unprecedented speed for the analysis of trace heavy metal ions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Trace heavy metal elements occur naturally in the earth's crust [1] and are inevitably discharged into the environment by either natural processes or human activities [2]. High levels of these

* Corresponding author.

E-mail address: yusun@mx.nthu.edu.tw (Y.-C. Sun).

metals in aquatic environments are well known to cause serious pollution problems and are toxic to a variety of ecosystems [3]. Conversely, some metal species are essential for certain physiological reactions, and enter the human body through the food chain [4]. However, excessive intake of these metals is harmful to human health [5]. Thus, from the viewpoint of environmental management and contamination prevention, the fast and accurate monitoring of the levels of trace heavy metals in natural water is of great importance.

Inductively coupled plasma-mass spectrometry (ICP-MS) is widely recognized as one of the most powerful methods for trace metal analysis by virtue of its superior analytical features, such as its wide linear dynamic range, its suitability for simultaneous multi-elemental and multi-isotopic analysis, and its ability to facilitate the ultrasensitive analysis of a large number of samples [6]. However, the effects of salt build-up and polyatomic interference remain problematic for accurate determination of trace metals in complicated matrices using ICP-MS instrumentation [7–9]. Thus, while raw samples are unsuitable for direct analysis, applying appropriate pretreatment procedures to the collected sample prior to ICP-MS measurement is indispensable [10].

Up to date, numerous sample pretreatment techniques, such as liquid–liquid extraction [11–13], solid-phase extraction (SPE) [14–18], and microwave digestion [19,20], have been successfully applied to the determination of trace heavy metals with ICP-MS instrumentation. Of these techniques, SPE is especially popular because both sample cleanup and analyte preconcentration can be accomplished simultaneously [21]. Recently, the development of small SPE-capable devices has surged due to their unique advantages, such as very low reagent/sample requirement, potential for multi-functionality, and so on, which benefit from downsizing the dimensions of analytical systems [22–25].

In 2010, a novel strategy involving the combination of a magnetic nanoparticle (MNP)-based SPE microchip and electrothermal vaporization (ETV)-ICP-MS for determining ultratrace levels of Cd, Hg, and Pb was proposed by Chen et al. [26]. MNPs modified with γ -mercaptopropyltrimethoxysilane (γ -MPTS) were packed into microchannels for the selective extraction of metal ions from cultured cells with the aid of an external magnetic field. Furthermore, a method for the determination of Cu using aminobenzyl ethylenediaminetetraacetic acid (ABEDTA)-coated magnetic microparticles (MMPs), a magnet-embedded poly(dimethylsiloxane) (PDMS) chip, and a graphite furnace atomic absorption spectrometer (GFAAS) has been described by Kim et al. [27].

In 2011, Shih et al. constructed an automated analytical system that coupled a functionalized poly(methyl methacrylate) (PMMA) SPE chip with ICP-MS for online determination of trace metal ions in volume-limited microdialysate samples [28]. The chip channel was used directly as an SPE sorbent for the collection of trace heavy metals, such as Mn, Co, Ni, Cu, and Pb, after simple hydrolysis treatment. Also, in 2013, Xue et al. integrated SPE preconcentration and fluorescence derivatization into a PDMS chip for the detection of Ca, Mg, Zn, and Pb [29]. The ion-exchange resins used for metal ion enrichment were cleverly held in place by fabricated microweirs, and the fluorescence-active reagent 8-hydroxy-quinolin-5-sulfonic acid (HQS) was online complexed with the metal ions for subsequent fluorescence detection. In 2014, Shih et al. introduced Cl-containing SPE functionality into a PMMA chip through photo-synthesis procedures [30]. Because this innovative extraction mechanism relied only on the dipole-electrostatic interaction between the channel surface and the metal ions, the volume of reagents required for SPE procedures and the periodic regeneration of extraction media were minimized.

In contrast to the combination of on-chip SPE techniques and conventional detection methods, a compact elemental analyzer

named on-chip liquid electrode plasma-atomic emission spectrometry (LEP-AES) has emerged in recent years [31]. In 2013, Khoai et al. attempted to integrate a resin-packed SPE unit with an on-chip LEP-AES system for the enhanced detection of Pb ions [32]. The SPE unit was formed by localizing commercial ion-exchange resins via slit-shaped barriers. Further improvements to the analytical performance of this system were made by slight configurational modifications in the following year [33].

In recent years, much progress in the development of on-chip SPE techniques has been reported. Although the success of such techniques has been realized in a variety of applications for trace metal analyses, the majority of research efforts has been directed toward the improvement of extraction efficiency, the reduction of reagent/sample consumption, and the integration of detection functionalities with on-chip SPE techniques. In contrast, very little research into the enhancement of analytical throughput has been conducted, even though analysis time is of huge concern in routine work. As highlighted by Papadoyannis and Samanidou [34], over 60% of analysis time is consumed by sample preparation, seriously prolonging the time needed for each analysis, and hampering the more widespread use of the on-chip SPE technique for routine analytical work. Therefore, a sample pretreatment method that provides not only excellent processing efficiency but also high analytical throughput is highly desirable.

In 2009, Lafleur and Salin reported the development of a novel centrifugal microfluidic device combined with laser ablation (LA)-ICP-MS for high-throughput analysis of metal ions, such as Co, Ni, Cu, Pb, and V [35]. Typically, metal ions were chelated with 8-hydroxyquinoline (8-HQ) in advance and then retained in gel-packed microchannels, followed by LA-ICP-MS analysis. In contrast to the usual methods for fluid manipulation in miniaturized systems, the sample/reagent solutions were driven by centrifugal force without the use of any other pumping equipment. Because several SPE units were integrated into a compact disc, each device could be used to process up to 8 samples simultaneously. Using this strategy, the time needed for each analysis could be dramatically decreased by increasing the number of integrated SPE units. However, the analytical throughput was enhanced by performing the analyses in parallel, but the time spent on pretreatment for each sample was essentially unreduced. Thus, the problem of limited analytical throughput caused by lengthy SPE procedures remains to be addressed.

In this work, a hyphenated system based on a new strategy for rapidly determining trace heavy metals was developed. Instead of the parallel procedures usually employed to expedite on-chip high-throughput analysis, a method involving the acceleration of individual sample processing by increasing the operation flow rate during SPE procedures was adopted. To overcome possible adverse effects, the integration of a micromixer and an ingenious multi-channeled extraction unit into the developed device was employed. Furthermore, full automation of the system was achieved by use of a programmable valve manifold as the interface combining the developed microchip and ICP-MS instrumentation. To the best of our knowledge, the hyphenated high-throughput SPE (htSPE) microchip system developed in this study can complete an individual analysis for trace heavy metal ions in significantly less time than other on-chip SPE techniques reported in the literature.

2. Experimental section

2.1. Chemicals and materials

All chemicals were of analytical reagent grade and used as received unless otherwise stated. Deionized water (DI H₂O, 18.2 M Ω cm) was obtained using a Milli-Q apparatus (Millipore,

Download English Version:

<https://daneshyari.com/en/article/1163007>

Download Persian Version:

<https://daneshyari.com/article/1163007>

[Daneshyari.com](https://daneshyari.com)