Talanta 88 (2012) 352–357

Contents lists available at SciVerse ScienceDirect

Talanta

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

Development of a miniature analytical system in a lab-on-valve for determination of trace copper by bead injection spectroscopy

Yong-Liang Yu[a], Ying Jiang[b], Rong-Huan He[a,*]

[a] Department of Chemistry, Northeastern University, Box 332, Shenyang 110819, China
[b] Research Center for Analytical Sciences, Northeastern University, Box 332, Shenyang 110819, China

ARTICLE INFO

Article history:
Received 14 September 2011
Received in revised form 27 October 2011
Accepted 28 October 2011
Available online 2 November 2011

Keywords:
Lab-on-valve
Miniaturization
Bead injection spectroscopy
Copper

ABSTRACT

A miniature analytical system based on a lab-on-valve platform is developed for trace metal analysis by bead injection spectroscopy. A multipurpose flow cell integrated into a lab-on-valve is furnished with two pieces of fiber optics to communicate with light source and charge coupled device (CCD) spectrometer, respectively, in order to monitor real-time absorbance of the samples. Micro-beads loaded with chromogenic reagent are packed into the multipurpose flow cell to form a renewable microcolumn for solid phase extraction by bead injection. When the sample solution flows through the microcolumn, the target analyte will be captured on the surface of beads and detected directly by the CCD spectrometer without elution. The beads are automatically discarded from the multipurpose flow cell after each analytical cycle. This analytical system was employed to determine trace copper by loading of a chromogenic reagent 2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene (zincon) on the beads of an anion exchanger (Sephadex QAE A-25). With a sample volume of 2.5 mL, a detection limit of 3 μg L^{-1} and a linear range of 10–100 μg L^{-1} were obtained for copper, along with a RSD value of 2.5% (at the 50 μg L^{-1} level). The accuracy and practical applicability of the proposed system were validated by analysing certified reference materials, i.e., GBW10010, GBW09101, GBW08608, and further demonstrated by spiking recovery of copper in a water sample.

1. Introduction

Trace metal/metalloid assay plays an important role in the field of analytical chemistry, especially to those of the highly toxic metal/metalloid species such as Cr(VI), Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg(I, II), Pb^{2+}, As(III) and Se(IV), which significantly impact on the ecological system, biological organisms as well as human health [1,2]. Atomic spectrometric methods, for example, atomic fluorescence spectrometry (AFS), electrothermal atomic absorption spectrometry (ETAAS), and inductively coupled plasma-mass spectrometry (ICP-MS), have inherently presented themselves as the most attractive option due to the excellent sensitivity and precision for the determination of trace levels of metal/metalloid species [3]. However, modern analytical systems require not only high detection sensitivity, precision and analytical throughput, but also the miniaturization and automation of analytical instrumentations [4–6]. The current commercial instrumentations are quite bulky and heavy, particularly for assessment of the adverse effects of trace metal/metalloid species in biological and environmental samples on the spot. Therefore, the development of portable analytical instruments is an effective supplement to current methods, especially for field analysis.

The lab-on-valve (LOV) concept proposed by Ruzicka in 2000 year has opened a new avenue in the miniaturization, automation and integration of on-line sample pretreatment and detection by means of the fact that a microconduit monolith is mounted atop a conventional multiposition valve (hence the name “lab-on-valve”) [7]. Due to the integrated multipurpose flow cell inside the valve, LOV is facilitated to employ various detection methods, such as absorption spectroscopy [4–6], fluorescence spectroscopy [8], electrochemistry [9–11], chemiluminescence [12], for real-time monitoring of the reactions taking place inside the flow cell. In the LOV system, the volume of the sample path from injector to detector and the generated waste can be minimized, which is suitable for the miniaturization of instrument. So far, several simple miniaturized analytical systems based on the LOV platform have been proposed and implemented for the determination of metal species, including spectrophotometric detection [4–6], electrochemical detection [9–11] and atomic spectrometric detection [13–15].

As a major sample-pretreatment approach inside the valve, bead-injection (BI) technique has presented a judicious advance towards automation and miniaturization, which has been implemented by in-valve manipulation of sorbent material to form solid-phase extraction (SPE) microcolumn in the microconduit unit

---

* Corresponding author. Tel.: +86 24 83688944; fax: +86 24 83676698.
E-mail address: herh@mail.neu.edu.cn (R.-H. He).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.10.052

of the LOV [16,17]. Analyte can be separated and preconcentrated from matrix components by various interactions with the active surface of the solid-phase material prior to the detection, such as electrostatic adsorption [18,19], chelating reaction [20,21], or hydrophobic interaction [22,23]. In addition, BI technique overcomes the drawbacks of the permanent packed-column by the renewable solid-phase material after each analytical cycle when required [24]. Analyte retained on the surfaces of SPE microcolumn can be directly detected by means of bead injection spectroscopy (BIS) without elution [25–27], or eluted from the surfaces of SPE microcolumn and transferred into the in-valve or external detector for measurement [28–31].

Based on BI technique and various in-valve detection methods, LOV-BI system has become a useful and independent analytical platform [25–29]. On one hand, BI technique offers the versatile in-valve sample pretreatment approach for routine assays and effectively improved the analytical performances. On the other hand, various in-valve detection methods provide the feasibility of LOV-BI system as a portable analytical instrument. The advantage of LOV-BI system served as a miniaturized analytical platform has been demonstrated in the biochemical assay [32–34]. LOV-BI system also has a potential ability for the determination of metal species, when beads with special functional groups are used for the selective capture of metal species and the measurement is subsequently employed by suitable in-valve detection methods.

We propose a miniaturized analytical system based on a LOV platform for trace metal analysis by bead injection spectroscopy. Micro-beads loaded with chromogenic reagent as a sensor are packed into the multipurpose flow cell of LOV by BI technique for selectively capturing metal species. In-valve spectrophotometric detection is carried out by the multipurpose flow cell furnished with optical fibers to communicate with an external light source and a CCD detector for measuring the absorbance of trace level metals. The target analyte retained on the surfaces of beads is directly detected by means of bead injection spectroscopy (BIS) without elution. Compared with the detection mode by elution and derivatization of analyte, the present approach is more flexible and simple during the operation. As a demonstration, trace copper analysis was made using this system. Micro-beads of an anion exchanger (Sephadex QAE A-25) loaded with a chromogenic reagent 2-carboxy-2′-hydroxy-5′-sulfoformazyl-benzene (zincon) were employed for the determination. Zincon has been extensively used for the determination of copper because of its favorable selectivity [35,36]. It can only react with a few of ions like copper and zinc. The interferences of the most common alkali metal ions and alkaline earth metal ions in the matrix salt species are eliminated. The target analyte of trace copper can be readily separated based on the variation of the stability of their zincon complexes with pH value. Distinct advantages in terms of sensitivity, selectivity and applicability have been presented by the present miniaturized analytical system.

2. Experimental

2.1. Apparatus

A FIAlab-3000 microSequential Injection System (FIAlab Instruments, USA) with LOV module was employed for the whole analytical manipulations, and configured as shown in Fig. 1. A syringe pump with capacity of 2.5 mL was used for fluidic delivery, which was connected to the center port of the LOV module via another end of the holding coil. The LOV module was mounted atop a six-port selection valve, incorporating a multipurpose flow cell connected to port 2 of the LOV module and all the other necessary flow channels. The optical path in the multipurpose flow cell was 10 mm long with the volume of 22 μL. Both ends of the optical path were furnished with two pieces of 600 μm i.d. fiber optics to communicate with a LS-1 tungsten halogen lamp (Ocean Optics, USA) as a light source and a USB2000 CCD spectrophotometer (Ocean Optics, USA) as a detector, respectively. In order to efficiently trap the beads within the optical path and allow the solution to flow through freely, the outlet of the multipurpose flow cell was equipped with a 10 μm polyethylene frit (Mo Bi Tec, Gottingen, Germany) which was stuck by a fiber-optic tip on the top and supported by a piece of 0.8 mm i.d. PEEK tubing at the bottom. Bead container made of 1 mL pipette tip was mounted on port 6, and the remaining ports were used for sample (port 5) and waste (port 4), respectively.

All external channels were 0.8 mm i.d. PTFE tubing connected to the LOV with PEEK nuts/ferrules. The capacity of the holding coil was ca. 3.0 mL. FIAlab software version 5.0 (FIAlab Instruments, USA) was used to control all of the system components as well as to collect data.

2.2. Reagents and samples

All the reagents used were at least of analytical grade and purchased from Sinopharm Chemical Reagent Co. (China-SCRC) unless stated otherwise. De-ionized water (18 MΩ cm) was used throughout the experiments. A stock solution of 1000 mg L^{-1} copper was prepared by dissolving appropriate amount of $CuSO_4 \cdot 5H_2O$ in 1% (v/v) HNO_3. The working standard solutions of copper were prepared daily by stepwise dilution of the stock solution with carrier solution. A stock solution of 1.6×10^{-2} mol L^{-1} zincon (2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene) was prepared by dissolving appropriate amount of solid reagent in 0.02 mol L^{-1} sodium hydroxide. The working solution of 4.0×10^{-4} mol L^{-1} fresh zincon was prepared by appropriate dilution of the stock solution with de-ionized water. An acetate buffer (pH 4.5) was prepared by dissolving 1.8 g anhydrous sodium acetate and 0.98 mL glacial acetic acid and diluting to 100 mL with de-ionized water. The acetate buffer of diluting 100 folds was used as carrier solution.

Sephadex QAE A-25 anion exchanger (40–120 μm) (Beijing Ruidahenghui Science & Technology Development Co., China) was used as the solid support for immobilization of zincon. Generally, approximate 80 mg of Sephadex QAE A-25 was weighed and added in 6.4 mL of 4.0×10^{-4} mol L^{-1} zincon solution. The mixture was soaked overnight, and then the beads were collected for bead injection.

The certified reference materials (CRMs) employed for the validation of the present system include GBW10010 rice, GBW09101 human hair and GBW08608 water, which were acquired from the National Center for Standard Materials. A previous pretreatment procedure was employed for digesting 0.1 g of GBW10010 rice and 0.1 g of GBW09101 human hair [15]. 10 mL of GBW08608 water was heated gently on a hot plate until the solution was nearly dried. All the above CRMs were finally dissolved and diluted with the carrier solution to 10 mL, 50 mL and 10 mL, respectively. In addition, a local riverine water sample (Dandong, China) was measured after addition of acetate buffer in the sample to 1% (v/v).

2.3. Operating procedure

A complete operating cycle includes the following steps:

Bead packing and equilibration: 650 μL of carrier solution at a flow rate of 200 μL s^{-1} and 12 μL of bead suspension at a flow rate of 20 μL s^{-1} were aspirated successively by SP from the carrier reservoir and port 6, respectively. The beads were afterwards dispensed by 300 μL of the carrier solution at a flow rate of 10 μL s^{-1} by SP through port 2, whereupon the beads were delivered and captured to form a solid-phase extraction column in the flow cell of LOV.

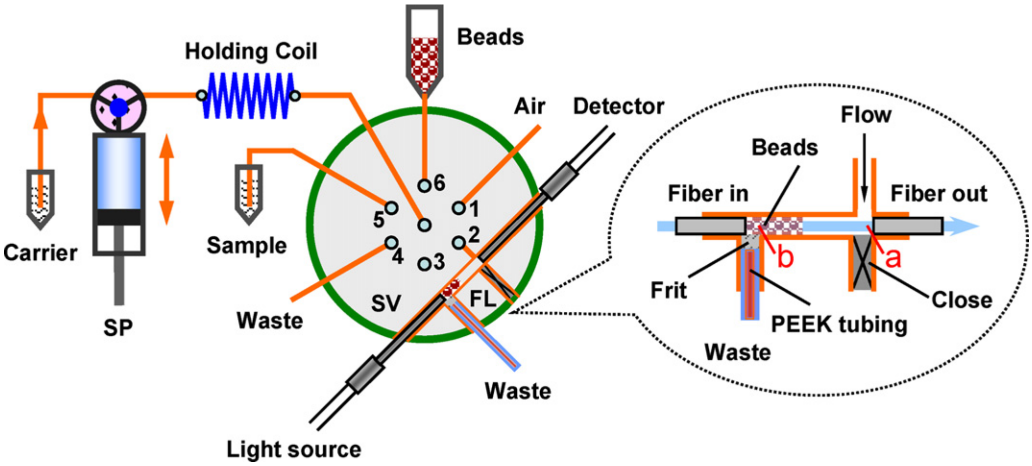

Fig. 1. Schematic diagram of the SI-LOV system incorporating a multipurpose flow cell for copper measurement by bead injection spectroscopy. SP: syringe pump; SV: selection valve; FL: multipurpose flow cell.

In the meanwhile, a large amount of the carrier solution flowed through the beads in order to reach the beads an equilibration.

Sample loading and measurement: Before the sample loading, beads packed in the flow cell of LOV were set as the reference of the sample measurement to deduct the background. 500 μL of sample solution was aspirated from port 5 at a flow rate of 200 μL s^{-1}. Thereafter, the sample solution followed by 50 μL of the carrier solution was dispensed by SP through port 2 at a flow rate of 10 μL s^{-1} to flow through the beads. The variations of absorbance in the flow cell were real-time monitored and recorded by the spectrophotometer in the whole process of sample loading. On changing samples, or whenever necessary, 200 μL of the sample solution to be detected was aspirated from port 5 by SP, which was afterwards dispensed to flow through port 4. This was followed by 200 μL of the carrier solution previously stored in the system to clean up the channels and remove possible residue of the previous sample solution in the conduit.

Bead discarding: After 25 s stopped flow, SP was set to aspirate 200 μL of solution remained in the flow cell together with the beads from port 2 at a flow rate of 20 μL s^{-1}, and then dispense them with 300 μL of the carrier solution via port 4 to the waste at a flow rate of 200 μL s^{-1} after each sample analytical cycle.

3. Results and discussion

3.1. Features of BIS in the LOV

The spectrophotometry as a simple and cheap technique has been extensively used for the determination of trace metals based on the reaction with different chromogenic reagents. However, the low sensitivity and sample matrix interferences remain inevitably the bottleneck of the entire analytical procedure. Preconcentration and separation of the analyte from the sample matrix are usually needed prior to the detection. The BIS approach provides an ideal alternative to overcome the drawbacks of the spectrophotometry [24]. Due to the preconcentration of the analyte in the bead surface, the sensitivity of the BIS is significantly higher than that of the corresponding spectrophotometry in liquid phase. Furthermore, the implicit separation of the analyte from its sample matrix is helpful to improve the selectivity under appropriate conditions.

The BIS approach has been achieved by using both batch [35] and flow modes [36], and the later mode has obvious advantage in the automation of sample pretreatment process, e.g. flow injection system or sequential injection system. Comparing to other flow modes, LOV system based on the unique features is more suitable for the operation of the BIS approach. The bead stock position and packing position are effectively connected by a microconduit monolith mounted atop a conventional multiposition valve, which extremely shortens the distance of bead transportation and decreases the risk of bead residual in the microchannel to ensure the reliability and repeatability of bead injection operation. The reagent consumption and waste generated are also minimized in the LOV. Meanwhile, the integrated multipurpose flow cell of the LOV is facilitated to realize real-time monitoring of bead spectrometry, which provides a miniaturized analytical platform. Therefore, LOV system was chosen to implement bead injection spectroscopy in this work.

3.2. Mode of bead packing and detection in the LOV

It is well-known that the transmittance in the solid phase bead is lower than that in liquid phase. Consequently, a relatively short distance (ca. length 1 mm, volume 2 μL) between the tips of the fiber-optic probes (i.e., the light path of the flow cell in the LOV) is generally chosen and beads are packed in the port (a) of Fig. 1 [25–27]. The amount of beads packed in the flow cell is limited by the space, which seriously restricts the retention capacity of solid phase microcolumn. Furthermore, a significant portion of beads remain inevitably outside the light path, which deteriorates the reliability and repeatability of the analysis. Therefore, a relatively long light path of the flow cell in the LOV was employed and beads were packed in the port (b) of Fig. 1. The relatively lager space, which can be detected, was used for packing more beads in the light path of flow cell in the LOV and improving the retention capacity.

3.3. Optimization of experimental conditions for copper detection

3.3.1. Effect of detection wavelength

When sample solution flew through the beads, copper reacted with zincon immobilized on the beads to form stable blue complex. Fig. 2 shows the variation of spectra before and after copper was retained onto the beads of Sephadex QAE A-25 loaded with zincon. According to the background spectra (line A in Fig. 2), it appeared that sufficient light was allowed to penetrate the bead layer in the range of 580–780 nm, which is important to implement the monitoring of absorbance in the medium of solid phase. In the meanwhile, the maximum absorbance wavelength was obtained around 600 nm (line B in Fig. 2) after the copper solution flew through the beads, which was just located in the suitable range of wavelength for monitoring of beads and was similar as that in

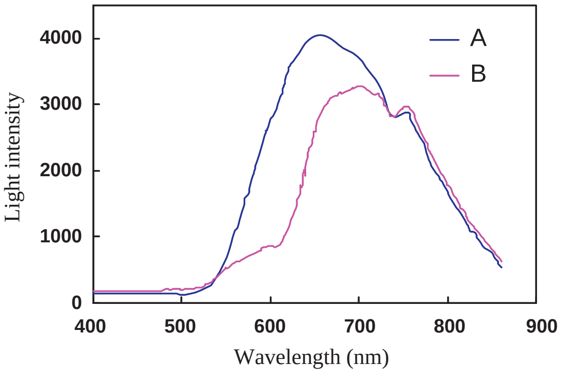

Fig. 2. Spectra of Sephadex QAE A-25 beads loaded with zincon: (A) background spectra of the beads; (B) spectra of the beads after sampling 500 μL of 0.4 mg L^{-1} copper in the acetate buffer of pH 4.5; sample flow rate, 10 μL s^{-1}.

liquid phase. Based on the highest sensitivity, 600 nm was set as the detection wavelength.

3.3.2. *Effect of beads*

The effect of beads on absorbance of copper was derived from two aspects, i.e. the amount of beads packed in the flow cell and the amount of zincon immobilized on beads. Due to the sufficient space that can be detected in the flow cell, the amount of beads packed was dependent on the retention capacity and sensitivity, as illustrated in Fig. 3A. When the amount of beads packed in the flow cell varied within a range of 6–18 μL, the absorbance of copper increased in the beginning and it was then declined with further increasing the amount of beads packed. The results indicated that the retention capacity was not enough in the condition of fewer amount of beads packed; nevertheless, the more packed beads resulted in insufficient light penetration through the bead layer and thus the decrease of sensitivity. Therefore, the amount of beads packed in the flow cell was fixed at 12 μL for further investigations. The amount of zincon immobilized on beads was also studied by varying the concentration of zincon solution within a range of 1.0×10^{-4} to 1.6×10^{-3} mol L^{-1}, as illustrated in Fig. 3B. The absorbance of copper significantly increased in the beginning and a maximum was reached at around 4.0×10^{-4} mol L^{-1}; a decline was observed by further increasing the concentration of zincon solution. Therefore, 6.4 mL of 4.0×10^{-4} mol L^{-1} zincon solution was used for soaking 80 mg of Sephadex QAE A-25 beads.

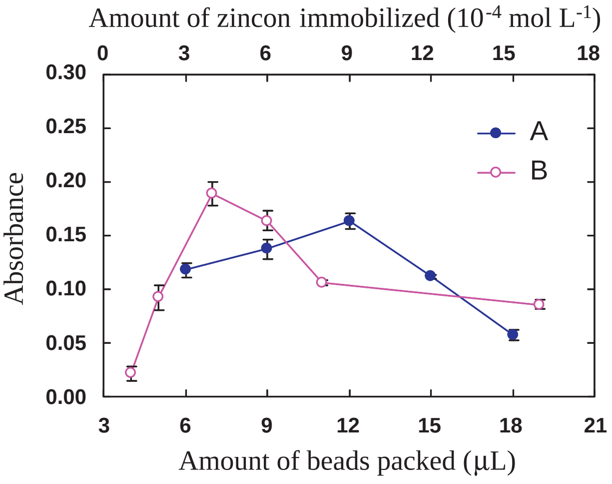

Fig. 3. Effect of beads on absorbance of copper: (A) varying the amount of beads packed in the flow cell; (B) varying the amount of zincon immobilized on beads. Sample volume, 500 μL; concentration of copper, 100 μg L^{-1} in the acetate buffer of pH 4.5; sample flow rate, 10 μL s^{-1}; detection wavelength, 600 nm.

Table 1
The characteristic analytical performance of the present system for the determination of trace copper.

Parameters	Protocol 1	Protocol 2
Sample volume	0.5 mL	2.5 mL
Sample frequency	21 h^{-1}	8 h^{-1}
Regressive equation	$A = 1.5404C + 0.0049$	$A = 8.8251C + 0.0006$
Correlation coefficient	$R = 0.9995$	$R = 0.9992$
Linear range	20–400 μg L^{-1}	10–100 μg L^{-1}
LOD (3σ, $n = 11$)	10 μg L^{-1}	3 μg L^{-1}
RSD ($n = 7$)	2.2% (200 μg L^{-1})	2.5% (50 μg L^{-1})

Beads packed in the flow cell as a sensor have good retention capacity under the conditions mentioned above, which has been demonstrated by the fact that a linear response of absorbance of copper was achieved by increasing the sampling volume up to 5 mL (0.05 mg L^{-1}). This important advantage is beneficial to improve the sensitivity of the system by preconcentration.

3.3.3. *Effect of pH value of the solutions*

The formation and stability of copper–zincon complex are dependent on pH value of the system. Therefore, the effect of pH value on absorbance was investigated by adjusting sample and carrier solutions with HCl or NaOH solutions in the range 2–10, as illustrated in Fig. 4 A. It was found that pH value within the range of 4–8 had very little influence on the signal of absorbance, while too low or too high pH value gave rise to a rapid drop of absorbance attributed to the decomposing or loss of copper–zincon complex from beads. In addition, the selectivity of the present procedure is also dependent on the pH value of the solution, and this issue will be discussed in Section 3.4. Considering the sensitivity and selectivity, the pH value of the sample and the carrier solution were controlled in the weak acid condition of pH 4.5 by the buffer solution.

3.3.4. *Effect of sample flow rate*

In a flow system, sample flow rate has a significant effect on the adsorption of analyte, which was thus investigated within a range of 5–25 μL s^{-1} as illustrated in Fig. 4B. The absorbance of copper gradually decreased with the increase of the sample flow rate. The phenomenon indicated that the kinetic adsorption process of copper on the beads was not instantaneous to be achieved. A lower flow rate was facilitated to improve the adsorption efficiency

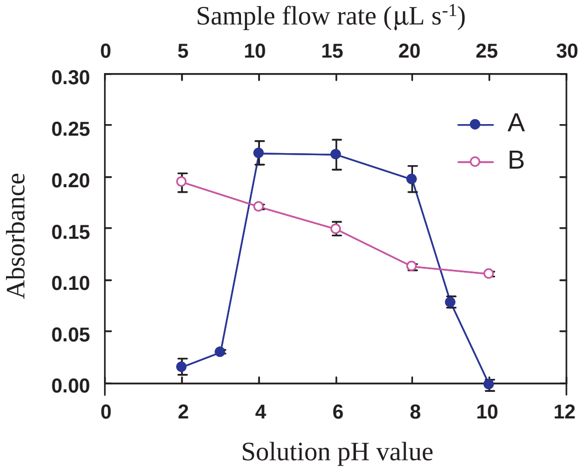

Fig. 4. Effects of solution pH value (A) and sample flow rate (B) on absorbance of copper. Sample volume, 500 μL; concentration of copper, 100 μg L^{-1}; detection wavelength, 600 nm.

Table 2
Determination of copper contents in various samples by the present system ($n = 3$).

Samples	Certified ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	Spiked ($\mu g\,L^{-1}$)	Recovery (%)
GBW10010	4.9 ± 0.3	4.5 ± 0.5	–	–
GBW09101	23 ± 1.4	22 ± 1	–	–
GBW08608	51 ± 2[a]	49 ± 2[a]	–	–
Riverine water	–	Not detected	50	96

[a] $ng\,g^{-1}$.

by the sufficient contact between analyte and adsorbent. However, too low flow rate will seriously restrict the analytical throughput. As a compromise, a sample flow rate of 10 $\mu L\,s^{-1}$ was finally selected for this system.

3.4. The effect of foreign ions

The potential interferences caused by several common cations and anions in the real samples were investigated by adding various amounts of possible interferences to the solutions of 0.1 $mg\,L^{-1}$ copper. The experimental results indicated that the tolerable ratio of each interfering ion concentration to 0.1 $mg\,L^{-1}$ Cu^{2+} prepared in the de-ionized water of pH 6.0 was 1000 for Na^+, K^+, Ca^{2+}, NO_3^-, Cl^- and Ac^-, 400 for Mg^{2+}, Cd^{2+}, Cr^{3+} and SO_4^{2-}, 100 for Al^{3+}, 50 for Fe^{3+}, 1 for Pb^{2+} and Mn^{2+}, 0.5 for Ni^{2+}, Zn^{2+} and Co^{2+} within the detection error range of ±5%. The high concentration of common anions, alkali and alkaline earth metal ions posed no obvious interferences, but the effects of some transition metal ions were not eliminated based on the selectivity of spectrum and micro-beads in the neutral condition. In order to improve the selectivity of the present system to copper, the sample solution needed to be controlled in the weak acid condition by the buffer solution. It was found that the tolerable ratio of Mn^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+} to 0.1 $mg\,L^{-1}$ Cu^{2+} prepared in the acetate buffer of pH 4.5 was significantly improved, i.e., 1000 for Pb^{2+} and Ni^{2+}, 100 for Zn^{2+}, 50 for Mn^{2+}, 25 for Co^{2+}. The contents of the aforementioned foreign ions in most of the real samples are well within the tolerant concentration range by using the present procedure. Therefore, no masking agents or further treatments were necessary.

3.5. Analytical performance of the system

Under the optimal conditions, the characteristic analytical performance data of the present system for the determination of trace copper were obtained and summarized in Table 1. With a sample volume of 0.5 mL, a detection limit of 10 $\mu g\,L^{-1}$ and a linear range of 20–400 $\mu g\,L^{-1}$ were obtained for copper. In the meanwhile, higher sensitivity of the present system was achieved by a larger sample volume (e.g. 2.5 mL) to meet the need of lower concentration analysis. Compared to the reported LOV systems for the determination of copper in liquid phase [5,6], the sensitivity of the present system is increased considerably due to the preconcentration effect of beads.

Fig. 5 illustrates the real-time variation of absorbance recorded for 0–400 $\mu g\,L^{-1}$ copper. A linear response of absorbance was recorded in the sampling process, and a plateau of absorbance was recorded after 25 s stopped flow. Due to the tight packing of beads during the sampling process, negative absorbance was shown in the beginning. In the meanwhile, a rise of absorbance after the sampling process was attributed to the recovery of pressure equilibration. It was found that 25 s stopped flow is enough to obtain the stable signal. Generally, the plateau value of absorbance is often used for quantitative analysis. However, the present system can provide another approach for quantitative analysis based on the slope of a linear response in the sampling process, which makes the measurement more flexible and simple. This slope value, defined as ΔA divided by Δt, is a linear function of the analyte concentration. The sampling volume or time can be flexible fixed based on the need of sensitivity, and no needs to be consistent with any calibration graphs.

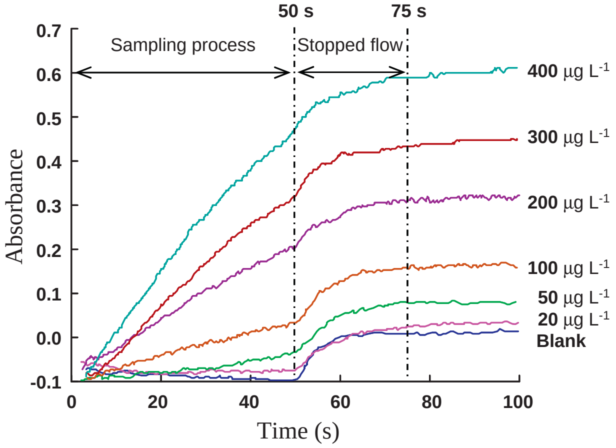

Fig. 5. Peak profiles obtained by the present system within the range 0–400 $\mu g\,L^{-1}$ copper under the optimized conditions.

3.6. Validation of the system

In order to evaluate the applicability of the present LOV-BIS system, it was applied to the determination of copper content in three certified reference materials, i.e. GBW10010 rice, GBW09101 human hair and GBW08608 water, and a local riverine water. The samples were pretreated with the methods described in Section 2.2, while the analytical results obtained are summarized in Table 2. It appears that the found values are in reasonable agreements with the certified values for all the three certified reference materials. Although copper is not found in the local riverine water due to the content below the LOD of the present system, the recovery obtained for the spiked sample is quite acceptable. These results indicate that the proposed method is sensitive and reliable for the determination of copper in real samples.

4. Conclusions

A miniaturized analytical system based on a LOV platform is developed for field analysis of trace metal by bead injection spectroscopy. Micro-beads loaded with the chromogenic reagent as a sensor are packed into the multipurpose flow cell of the LOV system for the capture and preconcentration of analyte, and sensitivity is thus significantly improved. The measurement of analyte is directly achieved by in situ spectrophotometric detection in solid phase without elution, which can overcome a series of problems due to the incomplete elution of analyte and provide a quantitative approach based on the slope by the real-time monitoring of absorbance. Since beads are automatically discarded and renewed before each analytical cycle, the quality of analysis can be guaranteed. In addition, the miniaturized LOV platform and its portability show promising practicability. In order to open a wider range of application, various novel sorbent materials as an optical sensor should be paid more attention. It is expected that the LOV-BIS technique will gain considerable momentum for metal species assay in the future.

Acknowledgements

This work is supported by the Natural Science Foundation of China (21005011, 21075013, 21005013, National Science Fund for Distinguished Young Scholars 20725517 and Major International Joint Research Project 20821120292), and the Fundamental Research Funds for the Central Universities (90105001, 100305003, 100305004, 100605002).

References

[1] G. Nabulo, S.D. Young, C.R. Black, Sci. Total Environ. 408 (2010) 5338–5351.
[2] X. Hu, Y. Zhang, J. Luo, T. Wang, H. Lian, Z. Ding, Environ. Pollut. 159 (2011) 1215–1221.
[3] O.T. Butler, J.M. Cook, C.M. Davidson, C.F. Harrington, D.L. Miles, J. Anal. Atom. Spectrom. 24 (2009) 131–177.
[4] M. Yang, J.-X. Li, J.-H. Wang, Talanta 72 (2007) 1710–1716.
[5] T. Leelasattarathkul, S. Liawruangrath, M. Rayanakorn, W. Oungpipat, B. Liawruangrath, Talanta 70 (2006) 656–660.
[6] S. Ohno, N. Teshima, T. Sakai, K. Grudpan, M. Polasek, Talanta 68 (2006) 527–534.
[7] J. Ruzicka, Analyst 125 (2000) 1053–1060.
[8] X. Chen, W. Wang, J. Wang, Analyst 130 (2005) 1240–1244.
[9] Y. Wang, Z. Liu, X. Hu, J. Cao, F. Wang, Q. Xu, C. Yang, Talanta 77 (2009) 1203–1207.
[10] Y. Wang, Z. Liu, G. Yao, P. Zhu, X. Hu, Q. Xu, C. Yang, Talanta 80 (2010) 1959–1963.
[11] Y. Wang, Z. Liu, G. Yao, P. Zhu, X. Hu, C. Yang, Q. Xu, Anal. Chim. Acta 649 (2009) 75–79.
[12] M. Yang, Y. Xu, J.-H. Wang, Anal. Chem. 78 (2006) 5900–5905.
[13] H. Erxleben, J. Ruzicka, Anal. Chem. 77 (2005) 5124–5128.
[14] Y.-L. Yu, Z. Du, J.-H. Wang, J. Anal. Atom. Spectrom. 22 (2007) 650–656.
[15] Y.-L. Yu, Z. Du, M.-L. Chen, J.-H. Wang, J. Anal. Atom. Spectrom. 23 (2008) 493–499.
[16] J. Wang, E.H. Hansen, M. Miro, Anal. Chim. Acta 499 (2003) 139–147.
[17] J. Wang, E.H. Hansen, Trends Anal. Chem. 22 (2003) 225–231.
[18] X. Long, M. Miro, E.H. Hansen, Analyst 131 (2006) 132–140.
[19] J. Wang, E.H. Hansen, Anal. Chim. Acta 424 (2000) 223–232.
[20] X. Long, E.H. Hansen, M. Miro, Talanta 66 (2005) 1326–1332.
[21] X. Long, M. Miro, E.H. Hansen, J. Anal. Atom. Spectrom. 20 (2005) 1203–1211.
[22] M. Miro, S. Jonczyk, J. Wang, E.H. Hansen, J. Anal. Atom. Spectrom. 18 (2003) 89–98.
[23] X. Long, R. Chomchoei, P. Gala, E.H. Hansen, Anal. Chim. Acta 523 (2004) 279–286.
[24] S.K. Hartwell, G.D. Christian, K. Grudpan, Trends Anal. Chem. 23 (2004) 619–623.
[25] J. Ruzicka, A.D. Carroll, I. Lahdesmaki, Analyst 131 (2006) 799–808.
[26] Y. Gutzman, A.D. Carroll, J. Ruzicka, Analyst 131 (2006) 809–815.
[27] M. Decuir, I. Lahdesmaki, A.D. Carroll, J. Ruzicka, Analyst 132 (2007) 818–822.
[28] H. Erxleben, J. Ruzicka, Analyst 130 (2005) 469–471.
[29] X.-W. Chen, Z.-R. Xu, B.-Y. Qu, Y.-F. Wu, J. Zhou, H.-D. Zhang, J. Fang, J.-H. Wang, Anal. Bioanal. Chem. 388 (2007) 157–163.
[30] J. Wang, E.H. Hansen, J. Anal. Atom. Spectrom. 16 (2001) 1349–1355.
[31] X. Long, M. Miro, E.H. Hansen, J.M. Estela, V. Cerda, Anal. Chem. 78 (2006) 8290–8298.
[32] M.D. Luque de Castro, J. Ruiz-Jimenez, J.A. Perez-Serradilla, Trends Anal. Chem. 27 (2008) 118–126.
[33] X.-W. Chen, M.-L. Chen, S. Chen, J.-H. Wang, Trends Anal. Chem. 27 (2008) 762–770.
[34] X.-W. Chen, J.-H. Wang, Anal. Chim. Acta 602 (2007) 173–180.
[35] P. Richter, M.I. Toral, H. Castro, Anal. Lett. 35 (2002) 635–646.
[36] M.J. Ruedas-Rama, A. Ruiz-Medina, A. Molina-Siaz, Anal. Sci. 21 (2005) 1074–1079.