Analytica Chimica Acta 976 (2017) 45–51

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

A miniature optical emission spectrometric system in a lab-on-valve for sensitive determination of cadmium

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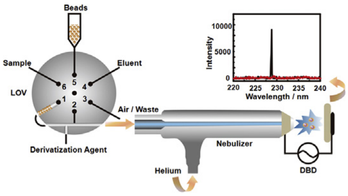
HIGHLIGHTS

- A miniature DBD-OES detection approach is firstly integrated in a LOV platform.
- It could readily achieve sample pretreatment, derivatization, nebulization and OES detection.
- It provides a technique for the detection of cadmium at a sub μg L^{-1} level.
- It is especially suitable for field analysis by virtue of small size.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 January 2017
Received in revised form
10 April 2017
Accepted 30 April 2017
Available online 13 May 2017

Keywords:
Miniature detection system
Dielectric barrier discharge
Lab-on-valve
Bead injection
Cadmium

ABSTRACT

A miniature optical emission spectrometric (OES) system is developed by incorporating dielectric barrier discharge (DBD) microplasma as excitation source in a lab-on-valve (LOV) configuration for trace cadmium analysis. The entire system integrates bead injection (BI) sample pretreatment, post-column derivatization, in-situ nebulization and OES detection. Trace cadmium in sample solution is separated and preconcentrated by flowing through a 2-(5-Br-2-pyridylazo)-5-dethylaminophenol (5-Br-PADAP) loaded microcolumn in LOV, followed by elution with 20 μL of 0.1 M hydrochloric acid. The eluate after online derivatization with 5 μL of 0.2 M borate buffer solution containing 7.5% (v/v) ethanol is immediately transported into a pneumatic micronebulizer integrating DBD microplasma for cadmium excitation, and OES is recorded by using a charge coupled device (CCD) spectrometer. As a miniaturized analytical set-up, LOV provides an ideal sample-processing front-end with detection by DBD-OES, while introduction of DBD excitation source in LOV highly improves the analytical performances for trace metal species. With a sample volume of 1.0 mL, a detection limit of 0.06 μg L^{-1} and a linear range of 0.2−50 μg L^{-1} are achieved for cadmium, along with an enrichment factor of 38. The accuracy of the present system is confirmed by the determination of cadmium in certified reference materials, and further demonstrated by spiking recoveries of cadmium in real water samples.

1. Introduction

Modern analytical instruments not only emphasize higher detection sensitivity and selectivity, but also focus on the features of automation, miniaturization and portability, especially for field analysis. The lab-on-valve (LOV) system [1,2], as the third-generation of flow-injection analysis technique, has exhibited an

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http://dx.doi.org/10.1016/j.aca.2017.04.055

excellent capability on microfluidic control, on-line sample processing and in-situ detection, since firstly reported in 2000 [3]. Based on the versatile LOV platform, the whole sample processing is readily achieved within a small integrated module prior to the subsequent detection, including on-line solution mixing, dilution, derivation, incubation, etc. So far, LOV as a miniaturized analytical system has been successfully applied for the determination of trace elements [4,5], organics [6,7] and biochemical substances [8,9].

Bead-injection (BI) technique [10], as a common sample processing approach, has been widely applied in the LOV platform for removing interfering matrix components and meantime preconcentrating the analyte on the active surface of the solid-phase microcolumn. LOV platform incorporating BI plays a positive role as a sample processing front-end with detection by various conventional analytical instruments, including atomic absorption spectrometry (AAS) [11], atomic fluorescence spectrometry (AFS) [12], inductively coupled plasma-mass spectrometry (ICP-MS) [13], gas chromatography (GC) [14], liquid chromatography (HPLC) [15], etc. For field analysis, a few integrated detection approaches for matching LOV as a miniaturized analytical system are also alternative, including spectrophotometry [16,17], fluorescence [18], chemiluminescence [19], electrochemistry [20], etc. However, LOV as a miniaturized analytical system remains underdeveloped in terms of detection sensitivity and alternative miniature detection approaches for accommodating various field analysis tasks.

Dielectric barrier discharge (DBD) microplasma, with the features of small size, stable discharge, low power consumption and nonthermal nature, provides a proper excitation source for the miniaturization of optical emission spectrometric (OES) detection [21]. It has been demonstrated that DBD microplasma could achieve the atomization and excitation of gaseous species or species in an aqueous medium, and the corresponding characteristic emission of element could be detected by a small spectrometer, e.g., charge coupled device (CCD), for quantification. Generally, the DBD-OES systems constructed for the determination of gaseous species [22] and those produced by electrothermal vaporization (ETV) [23] or chemical vapor generation (CVG) [24] are more sensitive than those for the direct determination of species in an aqueous medium [25,26], due to the limited atomization/excitation capability of DBD. However, in many cases analyte after a sample processing in a LOV system often exists in an aqueous medium, which greatly hampers the potential application of DBD-OES as an alternative miniature detection approach in LOV system for the determination of trace elemental species in solution. Recently, novel DBD microplasma integrated on a pneumatic micronebulizer was reported for the achievement of highly sensitive determination of cadmium in solution with a detection limit at the $\mu g\ L^{-1}$ level, which opens a promising avenue for the introduction of DBD-OES in LOV system [27]. It is noteworthy that an appropriate sample matrix is a critical factor for the improvement of the detection sensitivity of DBD-OES. In this respect, LOV platform incorporating BI with a powerful sample processing capability could readily achieve the matrix matching for the detection by DBD-OES. In the meantime, analyte preconcentration can easily be attained in a LOV platform, giving rise to further improvement of the detection sensitivity of DBD-OES.

In the present study, a miniature DBD-OES detection approach was, for the first time, integrated in a LOV platform for highly sensitive determination of trace heavy metal in environmental water. The present LOV system could achieve the required functions, including BI sample pretreatment, post-column derivatization, in-situ nebulization and OES detection. With cadmium as a model, the detection limit of the present LOV system could reach a sub $\mu g\ L^{-1}$ level. This provides a promising portable analytical system for fast and sensitive in field screening of trace heavy metal.

2. Experimental section

2.1. Reagents

All the reagents used in this work were at least of analytical reagent grade, and purchased from Sinopharm Chemical Reagent Co. (China-SCRC). De-ionized water (18 MΩ cm) was used throughout the experiments. A stock solution of 1000 mg L^{-1} cadmium was prepared by dissolving 0.5 g of spectropure cadmium powder in 15 mL of 50% (v/v) hot HNO_3 and diluted to 500 mL. The working standard solutions of cadmium were prepared daily by stepwise dilution of the stock solution with de-ionized water. 0.1 M of hydrochloric acid was used as an eluent, while 0.2 M of borate buffer solution containing 7.5% (v/v) ethanol was used as a derivatization agent. The beads (Cleanert PEP, 20–60 μm, Agela Technologies, China) for BI sample processing are preimpregnated in 0.5 g L^{-1} 2-(5-Br-2-pyridylazo)-5-dethylaminophenol (5-Br-PADAP) (Aladdin, China) ethanol solution for 6 h in advance. Deionized water was used as carrier solution. The purity of helium as carrier gas was more than 99.99%.

2.2. Sample pretreatment

The reliability and applicability of the miniature LOV-DBD-OES system was confirmed by the determination of trace cadmium in a series of water samples, including certified reference materials of GBW08608, BW085504, GBW(E)080196 and GBW(E)080082 (National Center for Standard Materials, China), riverine waters collected from Songhua River (Jilin, China) and Daqinggou River (Tongliao, China), Qipanshan spring water and snow water (Shenyang, China). The related information of certified reference materials and water samples are summarized in Table S1.

Considering the fact that HNO_3 in certified reference materials would seriously interfere with cadmium preconcentration and detection by the present system as detailed in “Matrix matching for the LOV-DBD-OES detection”, 4 mL of GBW08608 and 1 mL of BW085504, GBW(E)080196 and GBW(E)080082 were heated gently to near dryness for the removal of HNO_3. Then, all the samples were further diluted to 5 mL, 10 mL, 100 mL and 500 mL with 0.1 M borate buffer for ensuing detection, respectively. For each analysis, three replicates were performed for the elimination of error fluctuation. The found values were derived from the conversion of final concentrations of CRMs into their initial concentrations for comparison with the certified values. Real water samples were filtered through a 0.22 μm pore size membrane.

2.3. Instrumentation

The schematic diagram of the miniature LOV-DBD-OES system is illustrated in Fig. 1. The whole sample processing part of the present system was automatically manipulated by a common micro-sequential injection system (FIAlab Instruments, USA) furnished with a LOV module, a 6-port selection valve and two syringe pumps. A neon power supply (ENT-106B, Xinxing Neon Light Supply Company Ltd., Guangzhou, China) provided the energy for the generation of DBD microplasma, and a CCD spectrometer (AvaSpec-ULS2048-4-USB2, Avantes, Netherlands) integrating a fiber-optic probe (950 μm core i.d. and 20 cm length) and a 74-UV collimating lens (Ocean Optics, Dunedin, FL) was employed for recording the emission spectra. The different pH values of cadmium working standard solutions were adjusted using hydrochloric acid and sodium hydroxide by a pH meter (Thermo 868, Thermo Electron Corporation, USA). A commercial AFS instrument (AFS-9130, Beijing Titan Instruments Co., Ltd.) was used for the optimization of the concentration and volume of the eluent.