Abstract

Liquid electrode plasma optical emission spectrometry (LEP OES) is a novel analytical method employing the micro-discharge plasma generated in a liquid channel as an excitation source. LEP OES has advantages, for instance, no nebulizer required, battery-operated device, compactness and portability. However, LEP OES is not sufficiently sensitive to detect directly metal in low-concentration samples (ex. tap water and drinking water). Solid phase extraction (SPE) is a preconcentration method, which is used to increase analyte concentration prior to the detection. The analyte is firstly retained on a solid phase, and then is extracted to a mobile eluent in more concentrated form for quantitative determination. In the study, to improve sensitivity, LEP OES is combined with SPE. Accordingly, a SPE column is integrated on a LEP chip. The LEP is generated using direct current (DC) and alternating current (AC), which are named as DC LEP and AC LEP, respectively. Chip designs, performance protocols, data acquisition and data processing were proposed based on the investigated properties of each type of plasma sources. Lead was chosen as analyte of interest.

The chip for SPE-LEP combination containing a SPE column and a LEP channel was made by polydimethylsiloxane (PDMS) utilizing basic photolithography. The SPE resin was manually stuffed into the column using a syringe. Preconcentration was carried out with optimized parameters (sample volume and sample flow-rate). Then the eluent (ethylenediaminetetraacetate - EDTA 0.03 M) was applied through the resin to extract the ions of interest and transport them to LEP detection.

For SPE – DC LEP combination, a flow control technique with a pneumatic micropump was developed for fluid actuation. The design and fabrication of the pump were modified to be suitable with the integration. The pump is capable of providing an equalized volume of eluent for each LEP measurement cycle. Discharge volume of the pump is 90 nL with a relative error of 2%. Each small divided eluent requires a plasma generation and gives an emission spectrum. The emission intensities were fitted with exponential modified Gaussian (EMG) model. The fit curves are elution curves. The areas of the fit curves are proportional to the analyte amount that presents in the sample, thus they were used for quantitative determination of analyte (lead). With the proposed method, limit of detection (LOD) for lead was achieved as 0.4 µg/L (part per billion – ppb), 50 times improved compared to conventional LEP using quart chip. Sample volume used was 1 mL, and eluent volume was as small as 20 µL. The elution time was 40 minutes. The precision was improved compared to the method using syringe pump.

AC LEP has been developed for the first time in our study. Unlike DC LEP, AC LEP is capable of generating gently in the LEP channel at low flow-rate. Thus SPE – AC LEP were performed continuously. A buffer, the mixture of 0.1 M nitric acid and 5% v/v formic acid, was capable of maintaining the plasma for long time. During plasma generation, the eluent was introduced into the plasma by a syringe pump. The emission signals were obtained continuously, and then were fitted with EMG model. Similarly, the EMG fit curves were used to determine lead in the samples. LOD was obtained to be 0.5 µg/L (ppb) similarly with SPE – DC LEP. Sample volume used was 2 mL, and eluent volume was as small as 20 µL. The elution time was 8 minutes.

In conclusion, the integration of SPE into liquid electrode plasma for highly sensitive detection of lead has been successfully developed. Two types of LEP (DC LEP and AC LEP) were characterized. From the investigated characteristics, suitable chip layouts, fluid actuation techniques and data acquisition for the best combination LEP and SPE have been proposed. Generally, the sensitivity was improved about 50 times. SPE – DC LEP may offer a precise and sensitive method, while SPE – AC LEP offers a more simple and rapid method.

Keywords: Liquid electrode plasma, Solid phase extraction, Microfluidics chip, Elemental analysis, Heavy metal detection.