



## Original papers

## On-site detection of heavy metals in agriculture land by a disposable sensor based virtual instrument

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## ABSTRACT

A field-based detection system was designed and implemented for the simultaneous determination of heavy metals in soil samples. The detection principle is based on electrochemical differential pulse anodic stripping voltammetry (DPASV). In order to fulfill the requirements of field screening usage, a fast soil pretreatment process using ultrasonic-assisted extraction was applied. A disposable and integrated sensor, incorporating a three-electrode configuration (working electrode, reference electrode and counter electrode), was fabricated by the screen-printing technology and further modified with Nafion polymer and bismuth film. Coupled with the portable and flexible analysis instrument which was developed by virtual instrument technology, this system was used for trace determination of cadmium and lead content in soil. For accurate qualitative and quantitative analysis of heavy metals, the detection methodology based on the statistical algorithm and chemometrics method was proposed. The results showed that the system was sensitive, reliable and effective, which might hold great promise for its on-site analysis applications.

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## 1. Introduction

Lead and cadmium have been recognized as highly toxic heavy metals with serious effects on the human health (Kemper and Sommer, 2002). Unlike other pollutants, heavy metals tend to accumulate in environment because of their long-time chemical stability and nondegradable character. The heavy metals in soil can be absorbed by the crops and provoke a decrease in plant growth. Moreover, the accumulation of these pollutants in soil can enter the livestock or human bodies through food chain, which causes immediate or long-term poisoning. In recent years, the increasing demand for heavy metals screening has led to the need for rapid, decentralized analytical methods that can produce reliable results in field conditions (Pei et al., 2000; Metters et al., 2011).

Typical monitoring methods for trace metals in soil are realized by discrete collecting samples in field and transporting them to centralized laboratories for analysis. Several known techniques mainly based on spectroscopic principle, namely atomic emission spectroscopy (AES) Li et al., 2004, atomic absorption spectroscopy

(AAS) Báez et al., 2007 and inductively coupled plasma mass spectrometry (ICP-MS) Li et al., 2015, have been exploited for heavy metal determination. However, these methods are not suitable for in field application due to either time-consuming procedures, or complex sample pretreatment, or requirement of professional technicians and complex instruments (He et al., 2008). Electrochemical stripping analysis (ESA) has long been recognized as a powerful technique for measuring trace metals due to its remarkable sensitivity, fast speed, satisfactory selectivity and low cost. Nowadays, ESA has been widely applied to the determination of trace metals in food, beverage, water and other matrices (Economou, 2010). However, there are only few studies for analysis of metals in soil samples, especially for on-site application (Cooper et al., 2007; Palchetti et al., 2005; Ping et al., 2013; Christidis et al., 2007; Beni et al., 2005; Kadara et al., 2003; Beni et al., 2004; Kadara and Ibtisam, 2008). The major limitations for field soil analysis can be considered as follows: (1) *The reliable sensors*. Conventional electrochemical sensors are bulky, expensive and inconvenient, which need long time and complicated pretreatment before its use. Recent advances in electronics and micro-fabrication technologies have enabled the fabrication of minimal, disposable and ready to use sensors that named screen printed electrodes (SPE). However, the SPE is still faced some problems for soil application. It is partly attributed to the extremely low levels of heavy metals in

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natural environment, which makes the SPE suffer from the insufficient sensitivity for soil analysis. Furthermore, because of the high concentrations of organic matter and inorganic colloids in soil, the SPE signals of trace metals is often altered or even suppressed due to the absorption of those impurities onto the electrode surface. Therefore, special attention for the improvement of both sensitivity and anti-fouling ability of sensors should be paid before the soil analysis (Kefala et al., 2004). (II) *The suitable extraction methodology*. There are a lot of protocols have been designed for extraction of heavy metals in soil. In those protocols, long time mechanical-agitation steps (i.e., several hours) and large volume of reagents are commonly employed, which are unsuitable for the field implementation. Recently, the ultrasound-assisted extraction (UAE) has been proved to be a promising alternative technique that combines with the merits of simplicity, speed, economy and low reagent consumption. Despite such remarkable advantages, but so far, the number of publications using UAE coupled with electroanalytical for the detection of heavy metals in soil is still very limited (Calle et al., 2013; Kazi et al., 2006; Hwang et al., 2007). (III) *The appropriate instruments*. As noted above, only few studies for analysis of heavy metals in soil by ESA have been explored. In addition, most of those are carried out on the commercial electrochemical workstations, which are bulky, complicated and unsuitable for the outdoor deployment. Christidis and Beni have reported their single-chip controlled portable analyzer for the in-field measurement of Pb, Cd or Cu (Christidis et al., 2007; Beni et al., 2005). Nevertheless, these instruments are limited by their weak data handling capability and deficient performance, which result in a relatively high limit of detection (PPM level). Recently, the developments of “virtual instrument (VI)” technique have made it possible to fabricate the flexible instruments that combine the complex functionality with compact and inexpensive hardware.

In this work, a comprehensive study of field-based usage of ESA for the rapid screening of lead and cadmium in “real” soil is presented. A disposable and integrated SPE was fabricated by screen-printing technology and further modified with Nafion polymer and bismuth film. To the best our knowledge, this is the first reported use of this sensor for the determination of heavy metals in soil. Besides, a high performance yet portable detection instrument was also developed by the virtual instrument technique. Compared with the commercially available device, the major benefit of this instrument is that the analysis methodology is embedded in the software so that a simple and non-specialist operation is achieved. Combined with the portable instrument, the disposable SPE sensor as well as the fast UAE protocol, a novel integrated technology for the on-site measurement of heavy metals in soil is proposed. This system can be easily operated in field conditions with the advantages of fast speed, high precision and sensitivity, low operational cost as well as minimum physical dimensions.

## 2. Soil sample preparation

The soil samples were collected from some regions with cultivated lands (China), which are near highways or industrial areas. The extraction process was operated as follows: First, dried soil samples were grinded in a pestle and mortar, and further sieved by a 200  $\mu\text{m}$  sieve. A portion (1 g) of soil was placed in an extraction tube with 40 ml of 0.11 M acetic acid was added. The mixed sample was then exposed to ultrasonic bath for 1 h. The power of ultrasound can increase the extraction rate in the liquid media by provoking the “cavitation effect”, which releases a large amount of energy in the form of high temperature, extreme pressure as well as shock waves. Krasnoděbska-Ostrěga et al. have verified that 1 h ultrasonic-assisted extraction for soil sample can completely replace the 16 h EU standards BCR (European Union Community

Bureau of Reference) agitation extraction protocol (Krasnoděbska-Ostrěga and Kowalska, 2003). After extraction, the sample solution was filtered twice by the 0.22  $\mu\text{m}$  pore size filters. Prior to the test, the pH of the obtained extracting solutions was adjusted to 4.5 by using NaOH solution.

## 3. Sensor development

### 3.1. Electrode fabrication

Screen-printed electrodes were prepared by screen printing printer. The brief fabrication process is as follows: First, carbon ink is printed onto a flexible polyester substrate through a 200  $\mu\text{m}$  screen mesh for a working electrode (disc of 3.0 mm diameter) and a counter electrode. Next, the silver/silver chloride ink is printed on substrate for the reference electrode. Last, the epoxy insulation paste is covered on the electrode strip except the electrical connection and sensing part. The electrode is then heated to 80 °C for 2 h to evaporate off solvents. The configuration and photograph of the fabricated electrodes are shown in Fig. 1.

### 3.2. Electrode modification

For increasing the anti-fouling ability of SPE, a Nafion polymer was modified onto the SPE by dropping 5 ml of Nafion solution (5 wt.% solution) onto the surface of working electrode and then leaving to evaporate at room temperature for 10 min. Nafion is a cation-exchange polymer. It forms a protective permselective membrane on the surface of sensors. This membrane can exclude bulkier macromolecular and impurities from reaching the electrode surface by mechanical blocking, while makes the smaller metal cations pass through smoothly (Gouveia-Caridade et al., 2006). Besides, the additional advantages associated with the use of Nafion are providing the ability of pre-concentrating metal ions and enhancing the mechanical stabilization of sensors (He et al., 2008).

For improving the sensitivity of sensor, an “environmentally friendly” modified material – bismuth was applied. Traditionally, mercury is employed for increasing the sensibility to heavy metals of sensor, which is obviously unsuitable for the on-site utilization due to its high toxicity (Economou and Fielden, 2003). Recently, bismuth has been shown to offer a comparable performance to mercury (Wang et al., 2000). In this case, an “in situ” modified strategy for bismuth is applied. That means the bismuth ions are directly added into the testing solution and the bismuth film is electroplated onto the electrode surface during the analysis

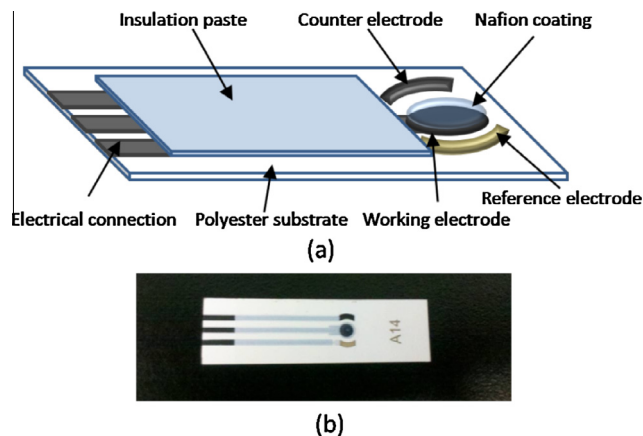


Fig. 1. (a) Schematic view of the SPE sensors, (b) the photograph of the fabricated SPE.

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