RESEARCH PAPER

A portable instrument for on-site detection of heavy metal ions in water

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Abstract

Based on differential pulse voltammetry technology, we developed a portable and affordable instrument for on-site detection of trace heavy metal pollutants in liquid through a disposable plastic pipette. It mainly consists of a six-electrode electrochemical sensor which is integrated in the instrument. The pipette chip is equipped with a pump valve, and thus, it can avoid contamination. We have analyzed the sensitivity and specificity of the electrochemical sensor for heavy metal detection. Experimental results demonstrated that the limit of detection for Pb, Hg, Cu, and Zn was 2.2 ng/mL, 2.5 ng/mL, 15.5 ng/mL, and 10 ng/mL, respectively. The limit of quantification for them was 10 ng/mL, 25 ng/mL, 25 ng/mL, and 14 ng/mL, respectively. The correlation coefficient between peak current and the target heavy metal concentration was above 0.96. Finally, we have tested the analytical performance of the self-build instrument by measuring heavy metal ions in industrial wastewater and rainwater, respectively. Such an instrument is user-friendly for all users even for the common people, and we can envision its wide application in future heavy metal pollutant detection in groundwater, tap water, and supernatant of soil solution.

Keywords Heavy metal ions · Electrochemical sensor · Portable instrument

Introduction

With the development of industry, heavy metal pollution is widespread in water and soil. Consequently, heavy metals accumulate through water and crops, then enter the body through the food chain [1–4]. High concentrations of heavy metals can cause irreversible harm to human health [5, 6]. Research also shows that most heavy metals can move freely across the human placenta, and consequently, they will be transferred from mothers to young infants [7, 8]; the determination of its concentration is of great value in clinical diagnosis and biological research. Until now, although there are many methods applied for the detection of heavy metal pollutant in liquid (e.g., UV-Vis absorption spectroscopy [9, 10], inductively coupled plasma-optical emission spectrometry [11], atomic absorption spectrometry [12]) (see Table S1 in Supplementary Information (ESM)), unfortunately, most of them require well-trained professionals to operate the instrument.

Differential pulse voltammetry (DPV) involves applying amplitude potential pulsed on a linear ramp potential. In DPV, the base potential value is chosen when there is no faradaic reaction. The base potential is increased with same increments, and simultaneously, the current varied with the pulsed was recorded [13]. With the development of electrode modification and nanomaterial technology, electrochemical analysis was employed for the detection of heavy metals in liquid [14]. For example, Gavino and Sanna analyzed Cu, Pb, Cd, and Zn in honey by differential pulse anodic stripping voltammetry with Hg microelectrodes [15]. Shahbazi et al. measured the metal content in different brands of milk by differential pulse anodic and cathodic stripping voltammetry method [4]. Zhao' group proposed a system for heavy metal detection in soil. They

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used n-octylpyridinum hexafluorophosphate and graphene to modify a disposable screen-printed electrode, and detected trace Cd^{2+} ions by anodic stripping voltammetry [16]. Based on square wave anodic stripping voltammetry technique, Liu's group realized the detection of Pb, Hg, Cu(II), and Cd by applying L-cysteine-functionalized mesoporous $MnFe_2O_4$ hybrid nanospheres ($MnFe_2O_4$@Cys) as electrochemical sensor [17]. Zhang introduced a flexible tape-based superhydrophilic-superhydrophobic tape, and realized on-site monitoring of chromium, copper, and nickel by naked eyes [18]. Zhao's lab strengthened the laser-induced breakdown spectroscopy method for detection of heavy metal ions by improving the enrichment way of heavy metal in water with graphite and aluminum electrode, and found that the graphite enrichment method combined with plasma spatial confinement was more appropriate for online detection of industrial waste water [19]. Although there are other researches about the on-site monitoring of heavy metal ions, most of them focused on the algorithms [20], substrate surface modifying [21], and optical biosensor designing [22]. Bernalte et al. have developed an electrochemical methodology for detection of Pb^{2+}, Cu^{2+}, and Hg^{2+} in water based on square wave anodic stripping voltammetry, but it requires

10 mL of water sample at least [23]. Huang's lab also designed an automated electrochemical measuring equipment for online monitoring of heavy metal ions in water [24]. Whitesides' group built an inexpensive, handheld device that coupled with electrochemical analysis to "the cloud" using any mobile phone [25]. The sampling and monitoring procedures seem quite complex, although the device is very smart. To our knowledge, there is still lack of versatile portable instrument for on-site heavy metal analysis.

In this work, we have developed a portable instrument with a disposable electrode-printed (DEP) chip for heavy metal determination. The disposable plastic pipette design can avoid cross-contamination for successive detection of heavy metal ions in liquid sample. To validate its analytical performance, we have investigated the effect of electrode chip surface, limit of detection (LOD) for some typical heavy metal ions, the interference between heavy metal ions, and the analytical performance of multi heavy metal detection. Such an instrument can be constructed at a cost of less than US$160, and we believe that this portable and affordable instrument can promote the development of on-site detection of trace heavy metal pollutants in liquid.

Fig. 1 The photo of (A) the heavy metal detection instrument and the schematic for (B) the principle of pipetting sample into the instrument and how to detect the target heavy metal ions by electrochemical sensor. (C) The schematic and the photo of the six-electrode chip. W, working electrode; R, reference electrode; C, counting electrode
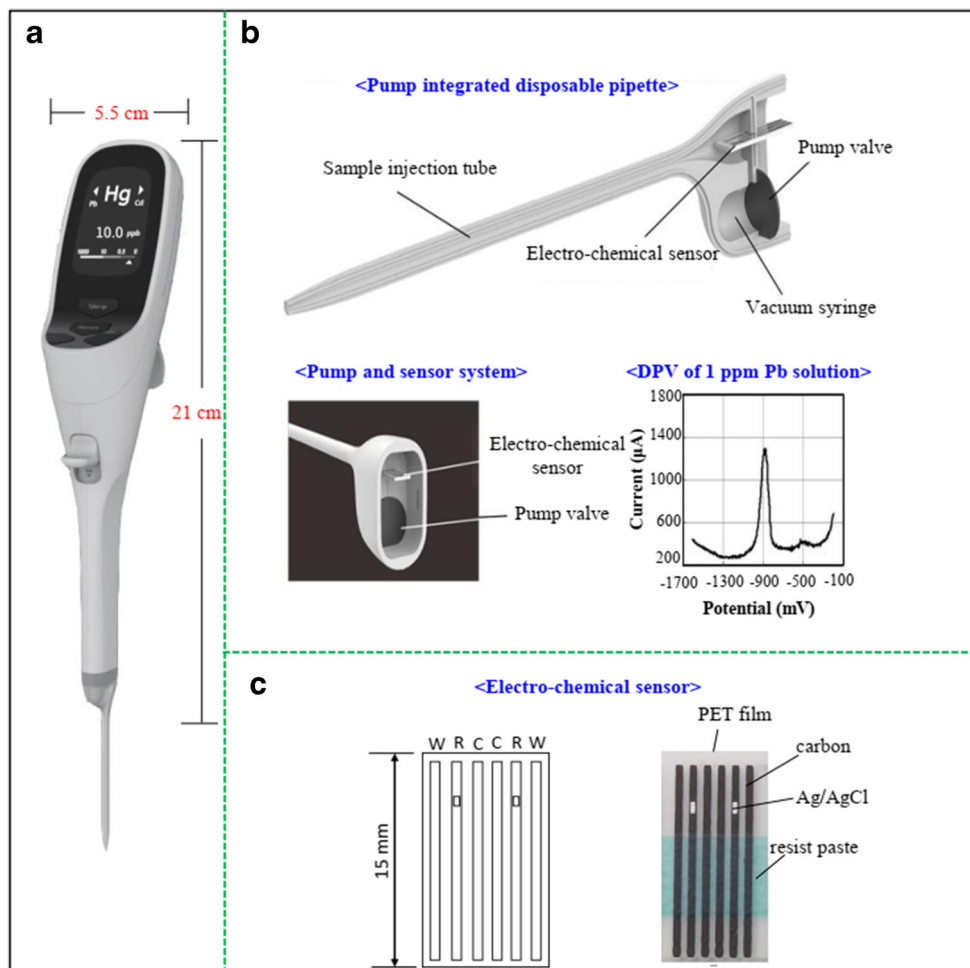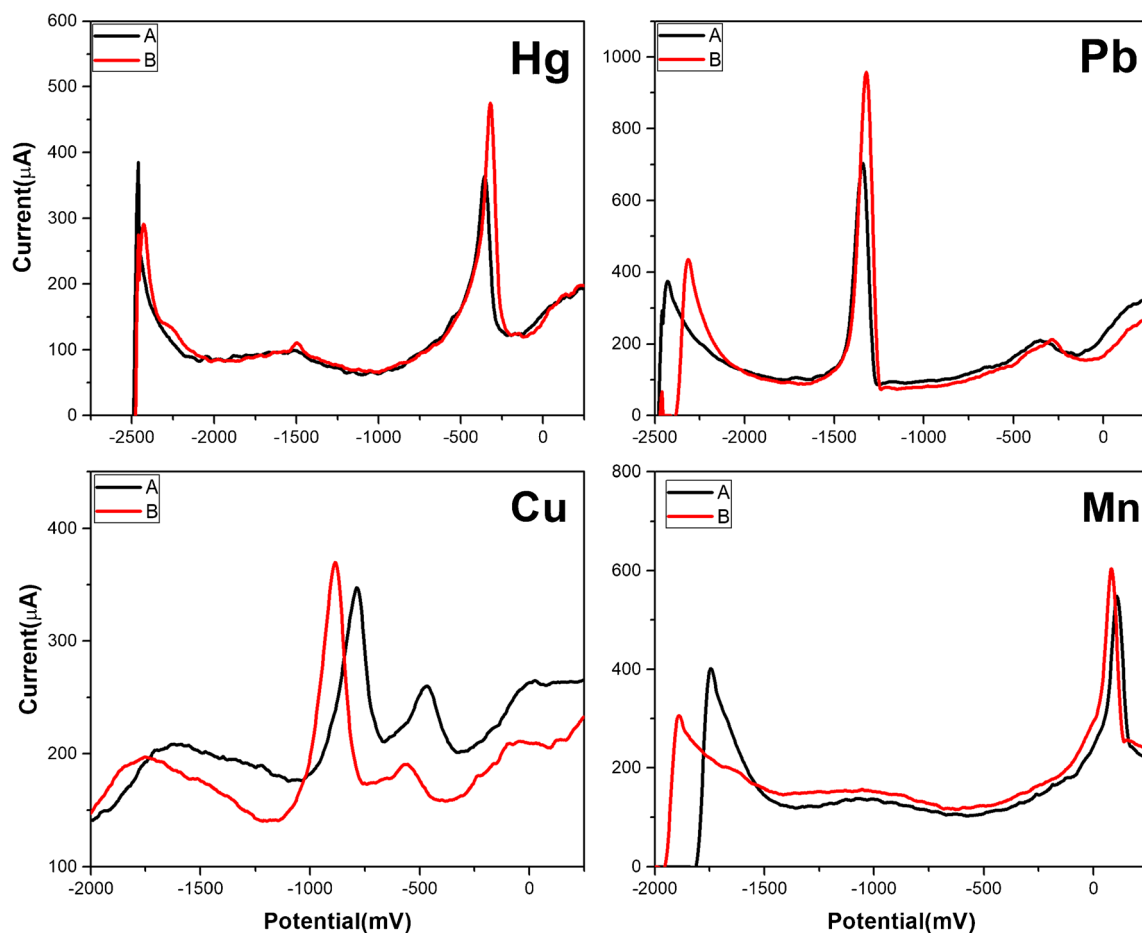
Fig. 2 The effect of electrode surface on the detection of Hg, Pb, Cu, and Mn. The sample was preconditioned at −2000 mV and for 120 s. The voltage is increased from −2500 to 250 mV at a rate of 20 mV/s

Materials and methods

Material and reagents

Standard solutions (1000 μg/mL) of Pb, Zn, Mn, Hg, and Cu were purchased from General Research Institute for Nonferrous Metals (Beijing, China). Deionized water was from ultrapure water system (Shanghai Xunhui Environmental Technology Co., Ltd., China). The DEP chips were supplied by Bio Device Technology Co. Ltd. (Ishikawa, Japan) and Yilong Bio. Co. Ltd. (Shanghai, China) based on screen printing technology. The chromium-rich polluted water was supplied by a Metal Processing Factory in Shanghai (China).

Fig. 3 The scanning electron microscopy photo of the two kinds of electrode
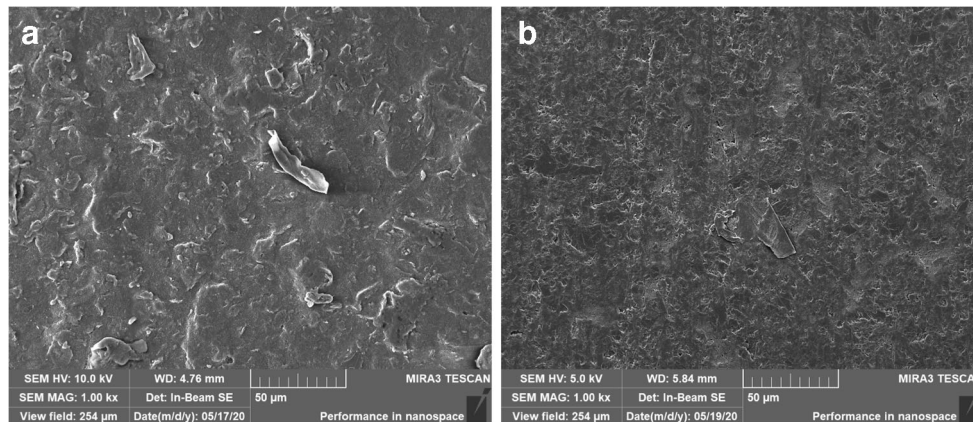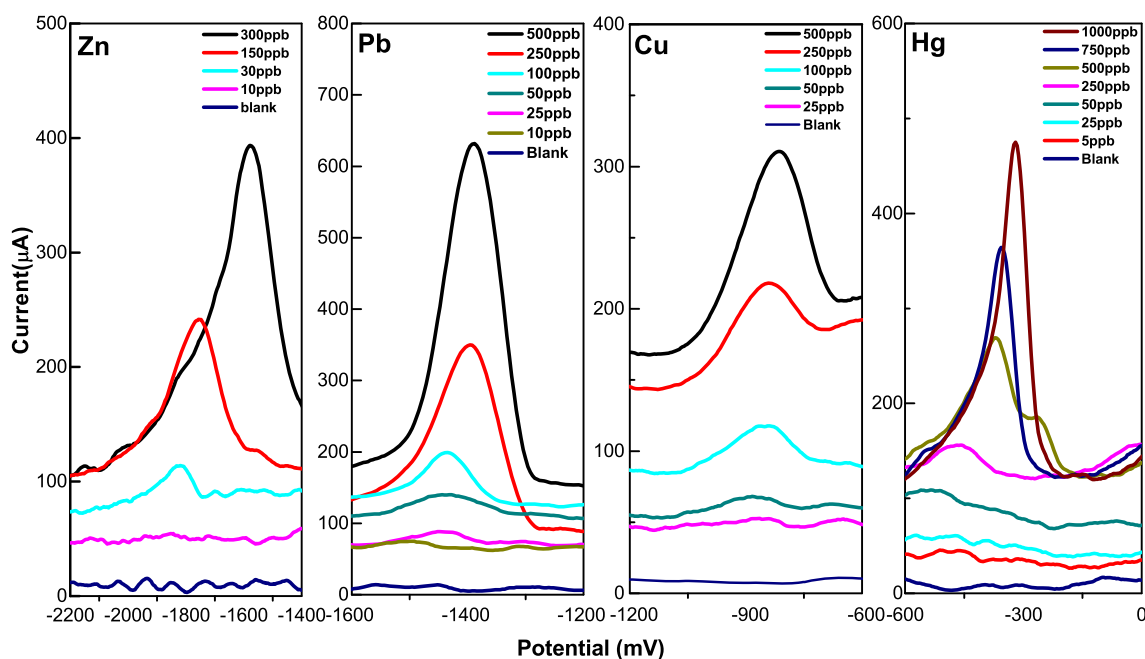
Fig. 4 The current varied with the scanning potential for Zn, Pb, Cu, and Hg, when the concentration of the sample was changed. The experimental conditions were as those in Fig. 2

System construction

The portable instrument for heavy metal detection was shown in Fig. 1A. It mainly consists of a disposable plastic pipette (Fig. 1B), a DEP chip (Fig. 1C), and the electronic circuit. The six-electrode DEP chip mainly includes two sets of Ag/AgCl reference electrode, carbon counter electrode, and carbon working electrode. The pump valve (see Fig.S1 in ESM) inside the instrument was made of rubber, and thus, it offered high elasticity for deformation. The basic working principle for this instrument is that when the user presses the pump valve, the volume of the tank will become small. Then if the button is released, the sample will be pipetted into the portable instrument and reach the surface of the electrochemical sensor. To observe the electric current varied with the scanning voltages, we also designed a portable heavy metal detection instrument with

industrial control panel (see Fig.S2 in ESM), and the software to demonstrate the current changed with potential was programmed by Microsoft Visual C# 2013. Global Tech Corp (Japan) manufactured the instrument for us.

Results and discussion

Effect of electrode surface

First, we evaluated the sensitivity of two kinds of DEP chips. To distinguish them, we named the electrode as A and B. The ratio of deionized water to standard solution is 1/999. They were equally divided into two identical parts, and thus, 1 μg/mL of Cu, Pb, Hg, and Mn of test samples were obtained. Then those four solutions were measured successively with potential from − 2000 mV at a scan rate of 20 mV/s, and the result was demonstrated in Fig. 2. It showed that there was a characteristic potential corresponding to Hg, Pb, Cu, and Mn, and the peak current by electrode B was obviously higher than it was by electrode A. To find the reason, we employed scanning electron microscopy (SEM, Tescan MIRA3) to get information about the morphology of the electrode surface. It demonstrated that the surface of electrode chip B was more uniform than that of electrode chip A (Fig. 3), which may make the metal cation easily deposit onto the active site of the electrode.
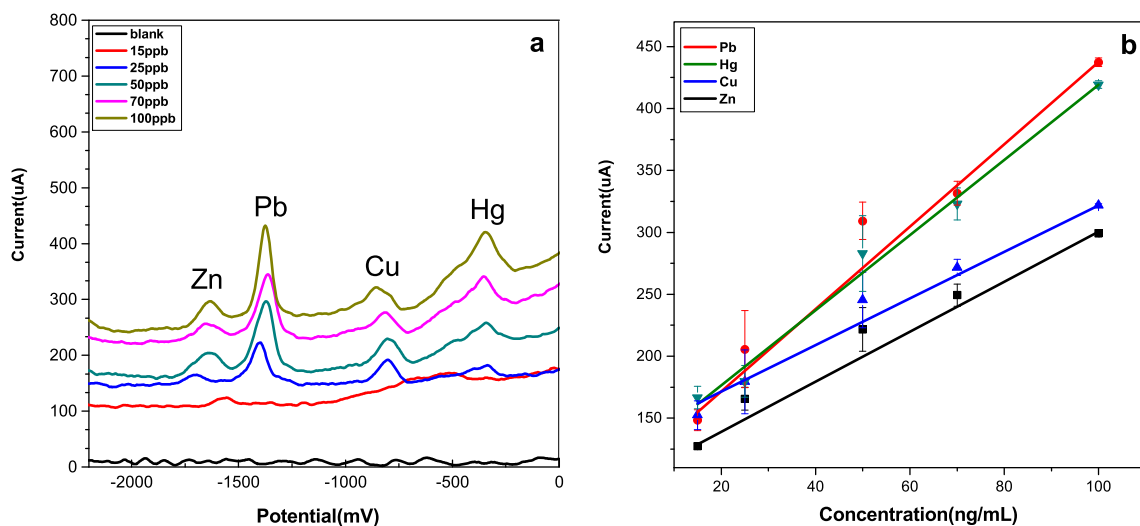
Table 1 The correlation coefficient for the heavy metal ions

	Slop	Intercept	R	LOQ (ng/mL)	LOD (ng/mL)
Zn	1.951	111.21	0.969	14	10
Pb	1.882	133.68	0.990	10	2.2
Cu	3.033	115.82	0.998	25	15.5
Hg	3.326	105.04	0.990	25	2.5

R, the correlation coefficient; *LOQ*, limit of quantification; *LOD*, limit of detection

Fig. 5 (A) Detection of multi heavy metals by the portable instrument and (B) the relationship between peak current and the concentration of the target heavy metal ions

Measurement of individual heavy metals

To determine the selectivity and sensitivity of the DEP chip, we have tested the common heavy metal pollutants (e.g., Zn, Pb, Cu, and Hg) based on the self-build instrument. The samples were diluted by deionized water, and the concentration of the test sample was varied from 5 to 1000 ng/mL. Each sample was preconditioned on the chip at -2000 mV for 120 s, and they were tested with electric potential from -2500 to 250 mV. All experiments were performed three times for reproducibility, and the result was demonstrated in Fig. 4. It showed that the characteristic potential peak for Zn, Pb, Cu,

and Hg was at about -1796 mV, -1471 mV, -816.06 mV, and -321 mV, respectively. The LOD for Pb, Hg, Cu, and Zn was 2.2 ng/mL, 2.5 ng/mL, 15.5 ng/mL, and 10 ng/mL, respectively. At the same time, limit of quantification (LOQ) for Pb, Hg, Cu, and Zn was 10 ng/mL, 25 ng/mL, 25 ng/mL, and 14 ng/mL, respectively. Moreover, the characteristic potential for Pb and Cu was nearly the same with the variation of its concentration, while for Zn and Hg, it was slightly increased with the growth of concentration. We also found that the peak current was linearly increased with the concentration of the heavy metal ions, and the correlation coefficients for all the calibration curves were higher than 0.96 (see Fig.S3 in ESM).
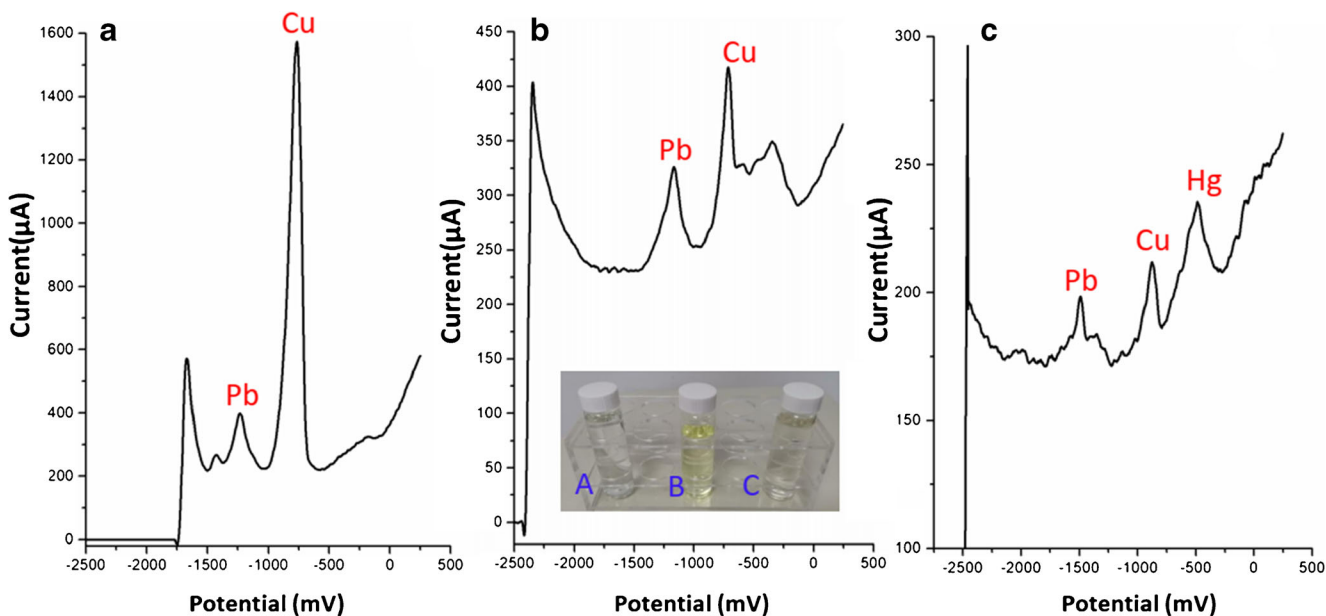

Fig. 6 Detection of (A) heavy metal ions mixed with industrial wastewater (B) industrial wastewater and (C) heavy metal ions mixed with rainwater. The insert in (A) demonstrated the photo of the wastewater sample. The experimental conditions were as those in Fig. 2

Interference between heavy metal ions

We then investigated the interference if there were two heavy metal ions in the liquid sample. Therefore, we measured two groups (A and B) of heavy metal solution based on the electrode-printed chip. In group A, there was about 250 ng/mL Pb, and the concentration of Cu was varied from 20 to 200 ng/mL. In group B, the concentration of Cu was 700 ng/mL, while the concentration of Pb was 90 ng/mL, 100 ng/mL, 150 ng/mL, 180 ng/mL, and 250 ng/mL, respectively. The volume of the test sample was 30 μL. It can be observed that the peak current increased with the concentration of Cu, while there was no obvious variation for the peak potential of Pb (ESM Fig.S4A), and vice versa (ESM Fig.S4B), indicating that there was no obvious interference for the characteristic potential of Pb and Cu (see Fig. S3 in ESM). The correlation coefficient (R) between concentration and the current was 0.970 and 0.948, respectively (see Fig.S5 in ESM).

Detection of multi heavy metals

Then we analyzed the solution containing Zn, Pb, Cu, and Hg based on the DEP chip, and the concentrations for them were 15 ng/mL, 25 ng/mL, 50 ng/mL, 70 ng/mL, and 100 ng/mL, respectively. The scanning potential was ranged from −2500 to 250 mV. Then those four solutions were measured by the self-built instrument in succession. Each experiment was performed three times for reproducibility. Data in Fig. 5A showed that there was nearly no obvious peak current if the solution contained no heavy metal ions, and the peak current increased with the growth of target heavy metal concentration. Furthermore, Fig. 5B demonstrated that there existed linearly relationship between the peak current and the concentration of Zn, Pb, Cu, and Hg. Detailed information about the fitting curves was tabulated in Table 1. However, we found that the peak current corresponding the same metal ion was higher than that in Fig. 4. This might because the signal of target metal ions experienced interference caused by co-deposition of other heavy metal ions onto the same active site of electrode surface.

Detection of heavy metal ions in real sample

Finally, we have applied the self-build instrument to detect the heavy metal ions in complex samples. The samples consisted of two kinds of industrial wastewater from a workshop (Metal Processing Factory, Shanghai) and rainwater, and the test sample was 30 μL. For industrial wastewater A, we found that there was an evident characteristic potential peak corresponding to Cu (Fig. 6A), and the characteristic potential peak corresponding the metal ions was observed after we added standard solution of 100 ng/mL Pb and 300 ng/mL Cu into the industrial wastewater B (Fig. 6B). Moreover, result showed that those target heavy metal ions were also observed by the self-build instrument after we added 100 ng/mL Pb, Cu, and Hg metal ions into the rainwater (Fig. 6C). We also found that the baseline will be elevated if the sample was complex by comparing the current from ultrapure water and rainwater (see Fig.S6 in ESM). To validate these heavy metal ions in the industrial wastewater and rainwater, we also compared the data measured by our instrument with it by ICP-OES (Optima 8000, Perkin-Elmer), which was demonstrated in Table S2 (see ESM), and it showed that the heavy metal ions detected by our instrument were slightly higher than the value if there were multi heavy metal ions in the waste water; the interference may be caused by the presence of other heavy metal ions on the active site of the electrode surface or other active ions from the sample, such problem may be overcome by applying pipette tips containing prefilter cartridge.

Conclusion

In summary, we have developed a portable heavy metal detection instrument based on a disposable plastic pipette and a DEP chip. Take Zn, Pb, Cu, Hg, and Mn as an example, we have performed series of experiments to validate the detection ability of liquid containing heavy metal ions. Results demonstrated that there was no apparent interference if there were Pb, Hg, Cu, and Zn in water. The LOD for them reached 2.2 ng/mL, 2.5 ng/mL, 15.5 ng/mL, and 10 ng/mL, respectively. To validate its utility, we tested the instrument by measuring the heavy metal ions in industrial wastewater and rainwater. Such an instrument is not only portable, but also requires only 30 μL liquid sample. Furthermore, it does not require professional training. Therefore, it may be of great value in the point-of-care test for heavy metal pollutants in liquid.

Declarations

Conflict of interest The authors declare no competing interests.

References

1. Shi T, Chen Y, Liu Y, Wu G. Visible and near-infrared reflectance spectroscopy-an alternative for monitoring soil contamination by heavy metals. J Hazard Mater. 2014;265:166–76.

2. Duruibe JO, Ogwuegbu M, Egwurugwu J. Heavy metal pollution and human biotoxic effects. Int J Phys Sci. 2007;2:112–8.

3. Shi T, Chen Y, Liu Y, Wu G. Visible and near-infrared reflectance spectroscopy—an alternative for monitoring soil contamination by heavy metals. J Hazard Mater. 2014;265:10.

4. Shahbazi Y, Ahmadi F, Fakhari F. Voltammetric determination of Pb, Cd, Zn, Cu and Se in milk and dairy products collected from Iran: an emphasis on permissible limits and risk assessment of exposure to heavy metals. Food Chem. 2016;192:1060–7.

5. Jing W, Miaosi L, Hua T, Jielong S, Minghui H, Guangxue C, et al. Portable paper sensors for the detection of heavy metals based on light transmission-improved quantification of colorimetric assays. Analyst. 2019;144:6382–90.

6. Duggal V, Rani A, Mehra R, Balaram V. Risk assessment of metals from groundwater in northeast Rajasthan. J Geol Soc India. 2017;90:77–84.

7. Ong C, Chia S, Foo S, Ong H, Tsakok M, Liouw P. Concentrations of heavy metals in maternal and umbilical cord blood. Biometals. 1993;6:61–6.

8. Majed A, Hassan A. Assessment of heavy and toxic metals in the blood and hair of Saudi Arabia smokers using modern analytical techniques. Int J Anal Chem. 2019;2:1–8.

9. Fedenko VS, Shemet SA, Landi M. UV–vis spectroscopy and colorimetric models for detecting anthocyanin-metal complexes in plants: an overview of in vitro and in vivo techniques. J Plant Physiol. 2017;212:13–28.

10. Nitoi I, Oancea P, Raileanu M, Crisan M, Constantin L, Cristea I. UV–VIS photocatalytic degradation of nitrobenzene from water using heavy metal doped titania. J Ind Eng Chem. 2015;21:677–82.

11. Sereshti H, Heravi YE, Samadi S. Optimized ultrasound-assisted emulsification microextraction for simultaneous trace multielement determination of heavy metals in real water samples by ICP-OES. Talanta. 2012;97:235–41.

12. Tüzen M. Determination of heavy metals in fish samples of the middle Black Sea (Turkey) by graphite furnace atomic absorption spectrometry. Food Chem. 2003;80(1):119–23.

13. Simões FR, Xavier MG. Electrochemical sensors. Nanoscience and its Applications. William Andrew Publishing; 2017.

14. Waheed A, Mansha M, Ullah N. Nanomaterials-based electrochemical detection of heavy metals in water: current status, challenges and future direction. TrAC Trends Anal Chem. 2018;105:37–51.

15. Sanna G, Pilo MI, Piu PC, Tapparo A, Seeber R. Determination of heavy metals in honey by anodic stripping voltammetry at microelectrodes. Anal Chim Acta. 2000;415:165–73.

16. Zhao G, Si Y, Wang H, Liu G. A portable electrochemical detection system based on graphene/ionic liquid modified screen-printed electrode for the detection of cadmium in soil by square wave anodic stripping voltammetry. Int J Electrochem Sci. 2016;11:54–64.

17. Zhou S-F, Wang J-J, Gan L, Han X-J, Fan H-L, Mei L-Y, et al. Individual and simultaneous electrochemical detection toward heavy metal ions based on L-cysteine modified mesoporous MnFe2O4 nanocrystal clusters. J Alloys Compd. 2017;721:492–500.

18. He X, Xu T, Gao W, Xu L-P, Pan T, Zhang X. Flexible superwettable tapes for on-site detection of heavy metals. Anal Chem. 2018;90:14105–10.

19. Meng D, Zhao N, Wang Y, Ma M, Fang L, Gu Y, et al. On-line/on-site analysis of heavy metals in water and soils by laser induced breakdown spectroscopy. Spectrochim Acta Part B: Atomic Spectroscopy. 2017;137:39–45.

20. Zhao G, Liu G. A portable electrochemical system for the on-site detection of heavy metals in farmland soil based on electrochemical sensors. IEEE Sensors J. 2018;18:5645–55.

21. Wang Z, Sun X, Li C, He X, Liu G. On-site detection of heavy metals in agriculture land by a disposable sensor based virtual instrument. Comput Electron Agric. 2016;123:176–83.

22. Long F, Zhu A, Shi H, Wang H, Liu J. Rapid on-site/in-situ detection of heavy metal ions in environmental water using a structure-switching DNA optical biosensor. Sci Rep. 2013;3:1–7.

23. Bernalte E, Arévalo S, Pérez-Taborda J, Wenk J, Estrela P, Avila A, et al. Rapid and on-site simultaneous electrochemical detection of copper, lead and mercury in the Amazon river. Sens Actuators B: Chemical. 2020;307:127620.

24. Lv Z-L, Qi G-M, Jiang T-J, Guo Z, Yu D-Y, Liu J-H, et al. A simplified electrochemical instrument equipped with automated flow-injection system and network communication technology for remote online monitoring of heavy metal ions. J Electroanal Chem. 2017;791:49–55.

25. Nemiroski A, Christodouleas DC, Hennek JW, Kumar AA, Maxwell EJ, Fernández-Abedul MT, et al. Universal mobile electrochemical detector designed for use in resource-limited applications. Proc Natl Acad Sci. 2014;111:11984–9.