A novel electrochemical sensor based on Co$_3$O$_4$-CeO$_2$-ZnO multi metal oxide nanocomposite for simultaneous detection of nanomolar Pb$^{2+}$ and Hg$^{2+}$ in different kind of spices

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Simultaneous and individual determination of Pb$^{2+}$ and Hg$^{2+}$ ions have been carried out based on the synergistic effect of Co$_3$O$_4$, CeO$_2$ and ZnO nanoparticles onto the carbon paste electrode. The morphology of synthesized nanocomposite (Co$_3$O$_4$-CeO$_2$-ZnO) has been investigated by Scanning Electron Microscope, Transmission Electron Microscope, X-ray diffraction and Fourier Transform Infrared spectroscopy. The voltammetric current has been increased linearly by increasing the concentration of Pb$^{2+}$ and Hg$^{2+}$ ions. The linear ranges of the Co$_3$O$_4$-CeO$_2$-ZnO/CPE sensor have been obtained 0.27–18.42 nM (for Pb$^{2+}$ ions) and 0.42–31.30 nM (for Hg$^{2+}$ ions), under optimum condition. The detection limits (3S$_b$/m) have been obtained 0.054 nM for Pb$^{2+}$ and 0.097 nM for Hg$^{2+}$, respectively. The proposed electrochemical sensor acts as a sensitive and selective method for simultaneous determination of two heavy metal ions and shows excellent repeatability, reproducibility, and stability, with relative standard deviation (RSD) less than 3%. Finally, Co$_3$O$_4$-CeO$_2$-ZnO/CPE has been successfully applied for the determination of Pb$^{2+}$ and Hg$^{2+}$ in different kind of spices.

Keywords: Electrochemical determination, Modified electrode, Co$_3$O$_4$-CeO$_2$-ZnO, Multi-metal oxide: Pb$^{2+}$, Hg$^{2+}$

In the last decade, some electrochemical sensors have been developed using several kinds of functional materials to improve selectivity, stability and the sensor response. The electrochemical sensors have been modified by functional materials. Theses material included various nano-materials such as metal nanoparticles (NPs), metal oxide NPs, polymeric NPs, carbon-based nanomaterials and quantum dots$^{1-5}$. A wide variety of nanocomposites have been recently applied to fabricate the modified sensors because of their biological compatibility, high-specific surface area, chemical stability, excellent catalytic activity and conductivity$^{6-13}$. These nanocomposites including metal oxide NPs and multi-metal oxide nanocomposites have been utilized as catalysts owing to their unique electronic structure. Hence, the synthesis of metal oxide nanocomposites has been investigated in order to evaluate their performance in different applications such as fuel cells, super capacitors, and electrochemical sensors$^{14-16}$.

Cobalt oxide (Co$_3$O$_4$) has recently aroused considerable interest due to the normal spinel structure owing to some advantages including energy conversion, storage, electrocatalytic properties, magnetic properties, high theoretical specific capacitance, low cost and low toxicity$^{17,18}$. In order to improve the electrochemical efficiencies of sensors, various nanostructures and synthesis of Co$_3$O$_4$ based material as a multi-metal oxide have been investigated$^{19,20}$. Cobalt oxide (Co$_3$O$_4$) is very attractive for oxidation catalysts’ preparation because of the presence of mobile oxygen in Co$_3$O$_4$. This means that the Co–O bond strength of Co$_3$O$_4$ is relatively weak, so reactive oxygen can be easily obtained from the lattice oxygen$^{21,22}$.

Cerium dioxide (CeO$_2$) NPs is one of the most interesting rare earth oxides. It is used in many chemical processes as an efficient catalyst and electronic booster, because of its high specific surface area, high conductivity, excellent redox performance, good mechanical strength and low-cost synthesis$^{23,24}$. Ceria has a high oxygen storage capacity and well-known catalytic and redox properties (couples of Ce$^{4+}$/Ce$^{3+}$), making more oxygen available for the oxidation process. The most important property is the oxygen storage and releasing capacity of CeO$_2$$^{25}$. In addition, the catalytic activity and electrochemical application of CeO$_2$ can be improved by mixing it with some metal oxides or metals$^{26,27}$.
Zinc oxide (ZnO) is a metal oxide NPs. It is a good electron acceptor with high electron mobility. It can be used as an appropriate conducting layer in anodic stripping voltammetry (ASV) and inductively coupled plasma atom emission spectrometry (ICP-AES). Zinc oxide nanoparticles have gained their attraction as adsorbents for heavy metals due to their high surface area, low cost and extraordinary removal capacity. It is known that there are many hydroxyl groups on the surface of ZnO NPs, resulting in coordination interaction between heavy metal ions and hydroxyl groups, so ZnO NPs can be used as the adsorbents of heavy metal ions. However, the poor conductivity of ZnO has limited its application in electrochemistry.

The synergetic effects of composite nanomaterials can differentiate their catalytic performance from each one of the components. The composition and morphology of metal oxide NPs are controllable, and the lattice matching between metal oxides can be easily realized. Thus, metal oxides are suitable for support matrices. Several kinds of nanocomposites have been synthesized with two or three different metal oxide NPs, which have high specific surface area and catalytic activity. Recently, the novel properties of multmetal oxides nanocomposites have been considered which are suitable for microelectronic devices, catalyst and semiconductor devices. There are many types of research carried out for the synthesis of bimetal-oxide nanocomposites such as Co3O4-CeO2, CeO2-ZnO, Co3O4-ZnO, and ternary metal oxide nanocomposites such as Co3O4-CeO2-ZnO.

According to the previous studies, heavy metal ions are not biodegradable, so these ions remain in the ecological systems and food chain indefinitely. Among heavy metal ions, mercury (Hg2+) and lead (Pb2+) are well-known as toxic pollutants in the environments and ecosystems. Even low level of Hg2+ and Pb2+ can cause toxic effects such as cancer, nervous disease, kidney damage, reproductive toxicity, birth defects and skin rash. Owing to the wide usage of Hg2+ and Pb2+, these are some of the causes of worldwide environmental pollution.

According to the stated reasons, a simple and rapid detection of Hg2+ and Pb2+ is important in different types of real samples. There are different methods for individually and simultaneously determining of heavy metals including flame atomic absorption spectrometry, UV-vis spectrometry, electrothermal atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and also electrochemical methods such as anodic stripping voltammetry (ASV) and also electrochemical methods such as anodic stripping voltammetry (ASV). Among the stated analytical methods, the electrochemical methods and specially ASV have been accepted as one of the best methods for individually and simultaneously determining of heavy metal ions. This method has some advantages such as high sensitivity, selectivity, short analysis time, portability, low detection limit, simple fabrication and modification of working electrode. The fabrication of various mercury-free electrodes and their modification using different materials to improve the surface area, conductivity, selectivity and sensitivity of electrode has been carried out over the past years. The applications of carbon paste electrode (CPE) as a working electrode for determination of different analytes has increased significantly owing to its low cost, easily fabrication, flexible substrate for modification, high sensitivity and renewable surface.

Earlier reports demonstrated that SnO2/graphene composite modified on glassy carbon electrode could simultaneously detect some heavy metal ions. However, anodic stripping voltammetry helped in simultaneous detection of heavy metal ions, it was bounded in terms of detection limit, sensitivity and relative correlation coefficient. This was owing to the competition of Cd(II), Pb(II), Cu(II) and Hg(II) ions towards the limited number of active sites. The fabrication of modified electrodes for the simultaneous determination of Cd(II), Pb(II), Cu(II), and Hg(II) through differential pulse anodic stripping voltammetry (DPASV) accomplished a bismuth film on the surface of electrode by electrodeposition of bismuth onto an EG electrode and used it for the co-detection of As(III), Hg(II) and Pb(II). The benefit that resulted was the inhibiting any damages of electrode's film and it could be used for electrochemical and other analytical tests.

Liu et al. prepared a ZnO NFs-coated GCE, with Nafion acting as an adhesive, and applied it as a new sensor for heavy metal determination with SWASV. The graphene/CeO2 hybrid nanocomposite used in the development of modified electrodes for the simultaneous determination of Cd(II), Pb(II), Cu(II), and Hg(II) through differential pulse anodic stripping voltammetry (DPASV). An electrochemical sensor based on the use of CeO2 nanoparticles modified glassy carbon electrode (CeO2/GCE) was prepared and applied individually and simultaneously for the determination of Cu(II) and Hg(II). The DPASV results indicated that the CeO2 NPs based sensor exhibits good electroanalytical performance with two well-resolved voltammetric stripping peaks for Cu(II) and Hg(II). A sensitive Pb(II) sensor was also fabricated based on Co3O4/reduced graphene oxide/chitosan (Co3O4/rGO/
chitosan) nanocomposite modified glassy carbon electrode (GCE). The Co$_3$O$_4$/rGO material was synthesized through in situ growth of Co$_3$O$_4$ nanoparticles (NPs) on GO and subsequent hydrazine reduction process$^{49}$. An electrochemical platform for the detection of Pb(II) using porous Co$_3$O$_4$ microsheets was also introduced by Huang et al.$^{50}$.

In this paper, a selective sensing electrode has been introduced based on Co$_3$O$_4$-CeO$_2$-ZnO/CPE for the individually and simultaneously determination of Hg$^{2+}$ and Pb$^{2+}$ ions in different kind of real samples.

**Experimental**

**Chemicals and apparatus**

All reagents were of analytical grade and used as received without any further purification. All of the working solutions were prepared using double distilled water (DDW). Laboratory glassware were kept overnight in a 10% (v/v) HNO$_3$ solution and then rinsed with DDW. Graphite powder (10 µm average particle size) and pure paraffin oil were purchased from Merck. Co(NO$_3$)$_2$$\cdot$6H$_2$O, Zn(NO$_3$)$_2$$\cdot$6H$_2$O, Ce(NO$_3$)$_3$$\cdot$6H$_2$O and Na$_2$CO$_3$ were purchased from Merck company and used in order to synthesise Co$_3$O$_4$-CeO$_2$-ZnO nanocomposite. Stock solutions of Pb$^{2+}$ and Hg$^{2+}$ (1000 mg L$^{-1}$) were prepared by dissolving appropriate amounts of HgCl$_2$ and PbCl$_2$ (Merck) in DDW, respectively. Britton-Robinson (B-R) buffers (pH 2–7) were prepared and they were tested as supporting electrolytes. Different real samples were purchased from the local market.

Behpajoh potentiostat/galvanostat system (Model BHP-2065-Iran) was used for all the electrochemical experiments. The electrochemical cell was assembled with a conventional three-electrode system A platinum wire, an Ag/AgCl/KCl (3 mol L$^{-1}$) electrode, modified or unmodified CPEs were employed as an auxiliary electrode, a reference electrode and working electrodes, respectively. The prepared nanocomposite was characterized by TEM images (Zeiss EM902A), XRD (38066 Riva, d/G. Via M. Misone, 11/D (TN)) and FT-IR (Perkin-Elmer, spectrum 100, FT-IR spectrometer). pH adjustments were carried out using a Metrohm model 713 (Herisau, Switzerland) pH-Meter.

**Preparation of Co$_3$O$_4$-CeO$_2$-ZnO nanocomposite and Co$_3$O$_4$, CeO$_2$ and ZnO nanoparticles**

The Co$_3$O$_4$-CeO$_2$-ZnO tri-metallic nanocomposite was synthesized by co-precipitation procedure. In the first step, the solution of Co(NO$_3$)$_2$$\cdot$6H$_2$O and Zn(NO$_3$)$_2$$\cdot$6H$_2$O (each of the solution was 0.25 M) were mixed in a 1:1 molar ratio and stirred for 2 h at room temperature. In the next step, the solutions of 0.25 M Ce(NO$_3$)$_3$$\cdot$6H$_2$O and Na$_2$CO$_3$ (1 M) by same molar ratio were added to the previous solution. The solution was stirred for 3 h at room temperature. Finally, the precipitate was separated by centrifuge and washed by DDW. The obtained precipitate was dried in an oven at 90 °C for 1 h and at 200 °C for 3 h, respectively. To achieve the Co$_3$O$_4$-CeO$_2$-ZnO tri-metallic nanocomposite, the dried precipitate was sintered in a furnace at 450 °C for 5 h. In this stage, the nanocomposite was annealed at 950 °C for 10 h to convert carbonate to oxide sample. The Co$_3$O$_4$, CeO$_2$, and ZnO nanoparticles were also synthesized by the same method without addition of other ions.

**Sensor preparation**

The bare CPE was prepared by hand-mixing of a pure graphite powder and a certain amount of paraffin oil (ratio of 70:30 w/w) in an agate mortar.

To prepare the Co$_3$O$_4$-CeO$_2$-ZnO/CPE modified electrode, a 10% w/w portion of Co$_3$O$_4$-CeO$_2$-ZnO was mixed with 60% w/w graphite powder. It was dispersed in dichloromethane to well-mixing of the composite and was stirred until dichloromethane evaporated completely. Then the paraffin oil (30 % w/w) was added and mixed until the uniform paste was obtained. This paste preparation method was applied to provide a reproducible sensor after each surface polishing of the electrode. All amount of each paste was transferred into an insulin syringe and packed carefully to avoid possible air gaps and improve the electrode resistance. A copper wire (1.0 mm diameter) was inserted into the unmodified and modified electrode to establish the electrical contact.

**Analytical procedure**

Square wave anodic stripping voltammetry (SWASV) technique was used for determination of analytes under optimized condition. It was performed in a 20 mL electrochemical cell containing B-R buffer as a supporting electrolyte medium. Hg$^{2+}$ and Cd$^{2+}$ were deposited at the reduction potential of –0.75 V vs. Ag/AgCl for 110 s. Re-Oxidation of Pb$^{0}$ to Pb$^{2+}$ and Hg$^{0}$ to Hg$^{2+}$ were performed in anodic stripping step in the potential range of –0.8 to 0.5 V vs. Ag/AgCl. Before any measurement, in pre-conditioning step, a potential of 1.0 V vs. Ag/AgCl for 60 s was performed to ensure dissolution of the remaining deposits on the surface of Co$_3$O$_4$-CeO$_2$-ZnO/CPE. The pre-concentration and cleaning steps were done while the solution of the electrochemical cell was stirred. The peak currents were measured at potentials of about –0.41 and 0.18 V vs. Ag/AgCl for Pb$^{2+}$ and Hg$^{2+}$, respectively.
Samples preparation
The proposed method was applied for the determination of Pb\(^{2+}\) and Hg\(^{2+}\) in 22 different spices samples. The sample preparation was performed based on standard methods of Institute of Standards and Industrial Research of Iran. Each sample was individually milled and sifted. About 0.50 g of the samples were incinerated for 5 h at 500 °C in a crucible. After cooling, the incinerated sample was carefully moistened with 12 mL of concentrated nitric acid. The mixture was heated on a hotplate for 5 min and filtered through filter paper. The filtration was collected into a 50 mL volumetric flask and diluted to the mark with DDW\(^3\)

Results and Discussion
Characterization of synthesized nanocomposite
The morphology, structure, and size of synthesized materials were investigated by SEM and TEM. The SEM and TEM image of Co\(_3\)O\(_4\)-CeO\(_2\)-ZnO are shown in Fig. 1a and Fig. 1b, respectively. It is found that Co\(_3\)O\(_4\)-CeO\(_2\)-ZnO tri-metallic nanocomposite with the average size of about 17 nm (nanoparticles with diameters in the range of 8–25 nm) was synthesized by the co-precipitation procedure. It is noticeable that the synthesized method is efficient to prevent the aggregation of Co\(_3\)O\(_4\), CeO\(_2\), and ZnO nanoparticles. Hence, the synthetized nanocomposite has a high specific surface area.

To confirm the chemical structure of the synthesized nanocomposite, the FT-IR spectra of the Co\(_3\)O\(_4\)-CeO\(_2\)-ZnO tri-metallic nanocomposite (Fig. 1c) was recorded. The FT-IR spectrum of the nanocomposite illustrates the absorption band at about 3500, 1400, 1100, 1000, 820, 615 and 460 cm\(^{-1}\) which confirm the presence of O-H of the carboxylic groups, CO\(_3\)\(^{2-}\), C-O, O-H, Ce-O, Zn-OH, and Zn-O. This absorption bands indicate the effectively synthesis of Co\(_3\)O\(_4\)-CeO\(_2\)-ZnO multi-metallic nanocomposite.

The XRD patterns of Co\(_3\)O\(_4\)-CeO\(_2\)-ZnO nanocomposite, Co\(_3\)O\(_4\), CeO\(_2\) and ZnO nanoparticles are shown in Fig. 1d. The XRD pattern of Co\(_3\)O\(_4\) shows three peaks about 20 = 31.77°, 36.28° and 56.42° which matches well with the standard sample

![Fig. 1 — (a) SEM, (b) TEM, (c) FT-IR spectra of Co\(_3\)O\(_4\)-CeO\(_2\)-ZnO tri-metallic nanocomposite, and (d) XRD patterns of Co\(_3\)O\(_4\), CeO\(_2\), ZnO and Co\(_3\)O\(_4\)-CeO\(_2\)-ZnO nanocomposite.](image-url)
(JCPDS-ICDD 9-418). The XRD pattern of the Co$_3$O$_4$ nanoparticles illustrate some peaks about $2\theta = 28.5^\circ$, 33.09°, 47.46°, 56.42°, 59.10°, 69.37°, 79.13°, 76.79° and 88.55° which is matched with the standard sample (JCPDS-ICDD 43-1002). The XRD pattern of ZnO nanoparticles represents seven peaks about $2\theta = 31.77^\circ$, 34.27°, 36.26°, 47.46°, 56.42°, 62.99° and 69.10° which are adjusted with the standard sample (JCPDS-ICDD 36-1451). According to the obtained results of XRD pattern of Co$_3$O$_4$-CeO$_2$-ZnO tri-metallic nanocomposite, the positions of diffraction peaks are in agreement with the standard samples of Co$_3$O$_4$, CeO$_2$ and ZnO nanoparticles.

Voltammetric behavior of Pb$^{2+}$ and Hg$^{2+}$ on the surface of unmodified and modified electrodes

To explain the function of modifiers in the electrodes preparing process, the stripping voltammograms were recorded with different electrodes. Square-wave voltammograms of a solution containing 5.00 nM Pb$^{2+}$ and Hg$^{2+}$ in B-R buffer (pH = 4.5, 0.1M) at the bare CPE and Co$_3$O$_4$-CeO$_2$-ZnO/CPE by accumulation potential $–0.75$ V for 110 s in the potential range $–0.8$ to 0.5 V vs. Ag/AgCl are shown in Fig. 2.

Voltammograms of the solution at bare CPE exhibited no stripping peaks in used condition. After modifying the sensing layer of electrode with Co$_3$O$_4$-CeO$_2$-ZnO nanocomposite, the Co$_3$O$_4$-CeO$_2$-ZnO/CPE did not show any oxidation peak in the absence of the analytes. After adding each analyte, two distinct stripping peaks can be seen for Pb$^{2+}$ at $–0.404$ V and Hg$^{2+}$ at 0.183 V with the peak separation of 0.578 V vs. Ag/AgCl. This peak was attributed to facilitating electron transfer between Pb$^{2+}$ or Hg$^{2+}$ ions and Co$_3$O$_4$-CeO$_2$-ZnO/CPE. It is also owing to increasing of the surface area of the electrode. Based on these observations, the Co$_3$O$_4$-CeO$_2$-ZnO/CPE can be useful for determination of Pb$^{2+}$ and Hg$^{2+}$ ions in aqueous solution.

The response of modified electrode is dependent on many factors including pH of solution, accommodation potential, time, and the instrumental parameters of SWV. These parameters were optimized to achieve the best peak shape, maximum current, and the lowest detection limit.

Effect of pH on the response of modified electrode

The effect of pH on the current responses of 5.00 nM of Pb$^{2+}$ and Hg$^{2+}$ on the Co$_3$O$_4$-CeO$_2$-ZnO/CPE was investigated in the range of 2.0 to 7.0 by SWV. The results are shown in Fig. 3a. The stripping currents for the both analytes have been raised by increasing of pH up to 4.5 and the maximum oxidation peak current appeared at pH 4.5. The peak current was decreased by further increasing of pH; it may be owing to the ions hydrolysis. Hence, the pH of 4.5 was selected for subsequent experiment.

Effect of deposition potential, deposition time and instrumental parameters on the voltammetric currents

Sensitivity and detection limit depend on deposition potential, accumulation time and instrumental parameters hence optimization of these parameters is necessary.

The effect of deposition potential on the stripping response of 5.00 nM Pb$^{2+}$ and Hg$^{2+}$ ions were studied while the deposition potential was changed from $–0.6$ and $–0.9$ V vs. Ag/AgCl on Co$_3$O$_4$-CeO$_2$-ZnO/CPE under optimum conditions (Fig. 3b). The study represents that the electrode response increase gradually by changing the deposition potential up to $–0.85$ V vs. Ag/AgCl and accumulation time up to 110 s. On the other hand, the stripping responses for the both cations have decreased while the deposition potential was more negative than $–0.85$ V vs. Ag/AgCl, because of the reduction of other chemicals at these potentials. The hydrogen evolution was also started at such negative potentials. The background current was more than the other potential range. Hence, the potential of $–0.85$ V vs. Ag/AgCl was selected as an optimum deposition potential.

The effect of deposition time on the stripping responses of Pb$^{2+}$ and Hg$^{2+}$ ions was studied from 20 to 130 s with a deposition potential of $–0.85$ V, and it has been found that the oxidation response is increased by increasing of accumulation time up to 110 s.

Fig. 2 — SW voltammograms in the absence and present 5.00 nM of Pb$^{2+}$ and Hg$^{2+}$, on the surface of bare CPE, and Co$_3$O$_4$-CeO$_2$-ZnO/CPE.
110 s (Fig. 3c). This is owing to the fact that the longer collection time caused more Pb²⁺ and Hg²⁺ ions to get accumulated at the electrode/solution interface onto modified surface, hence current increases. It can be seen that after 110 s, the stripping currents becomes approximately constant owing to surface saturation6,7,51. Hence, the accumulation time of 110 s was selected and used as an optimum condition.

In order to obtain well-defined SWASV peaks and the best response, the voltammetric instrumental parameters such as voltage step, pulse amplitude, SW frequency and the resting time have been also optimized. The optimized parameters are shown in Table 1.

**Interferences studies**

The electroactive compounds that are present in the real samples might be a potential interference during the electrochemical determination of the analytes. Hence, the performance of the proposed modified electrode toward detection of Pb²⁺ and Hg²⁺ ions was evaluated in the presence of some potentially interfering ions of real samples.

SWASV were carried out in a solution containing 1.0 nM Pb²⁺ and Hg²⁺ ions in the absence/presence of various concentrations of each interference substances. The tolerance limit was taken as the maximum concentration of the interference elements, which caused a ±5% relative error or more. Interference impact of some anions and cations including Li⁺, Na⁺, NH₄⁺, Ag⁺, Mg²⁺, Ba²⁺, Sr²⁺, Mn²⁺, Cd²⁺, Cu²⁺, Ni²⁺, Ca²⁺, Al³⁺, Bi³⁺, As³⁺, I⁻, Br⁻, NO₂⁻, NO₃⁻, SO₄²⁻, and ClO₄⁻ were investigated. The obtained results as shown in Table 2, demonstrated that these external substances have no
interference on the stripping current of Pb\(^{2+}\) and Hg\(^{2+}\) ions (until > 500 folds). Hence, the Co\(_3\)O\(_4\)-CeO\(_2\)-ZnO/CPE can be applied for the determination of Pb\(^{2+}\) and Hg\(^{2+}\) ions in real samples containing different ions.

**Analytical performance of Co\(_3\)O\(_4\)-CeO\(_2\)-ZnO/CPE for determination of Pb\(^{2+}\) and Hg\(^{2+}\)**

Under the optimum condition, SWV were recorded for different concentration of Pb\(^{2+}\) and Hg\(^{2+}\) on the Co\(_3\)O\(_4\)-CeO\(_2\)-ZnO/CPE. When concentrations of the both analytes were simultaneously increased, two separated stripping peaks with two linear ranges of 0.27–18.42 nM and 0.42–31.30 nM for Pb\(^{2+}\) and Hg\(^{2+}\) were obtained respectively. The linear regression equations of Pb\(^{2+}\) and Hg\(^{2+}\) and coefficients of determination were 

\[
I_{pa} = 1.1551C_{Pb} + 0.2839 \quad (R^2=0.9986)
\]

and

\[
I_{pa} = 0.4988C_{Hg} + 0.319 \quad (R^2=0.9986),
\]

respectively (Fig. 4a and 4b). LOD of the modified electrode was calculated based on three times of standard deviation of the blank signals to calibration slope (3Sb/m). LODs were calculated 0.054 and 0.097 nM for Pb\(^{2+}\) and Hg\(^{2+}\), respectively.

For individual determination of each analyte, the concentration of Hg\(^{2+}\) was kept constant in 3.0 nM while concentration of Pb\(^{2+}\) was changed from 0.27 to 18.42 nM (Fig. 5a), and in the other samples, the concentration of Pb\(^{2+}\) was kept constant in 3.0 nM while concentration of Hg\(^{2+}\) was changed from 0.42 to31.30 µg L\(^{-1}\) (Fig. 5b).

It can be seen that their stripping peak currents rose linearly for Pb\(^{2+}\) and Hg\(^{2+}\) with the following linear regression equations and coefficient of determination:

\[
Pb^{2+} \quad I_{pa} = 1.1567C_{Pb} + 0.2624 \quad R^2 = 0.9983 \quad \ldots (1)
\]

\[
Hg^{2+} \quad I_{pa} = 0.4983C_{Hg} + 0.3032 \quad R^2 = 0.9987 \quad \ldots (2)
\]
The comparison of the calibration curves of Pb\textsuperscript{2+} and Hg\textsuperscript{2+} in both individual or simultaneous determination shows that two analytes have no interfere with each other and the stripping current values are entirely similar at same concentrations. Hence, Co\textsubscript{3}O\textsubscript{4}-CeO\textsubscript{2}-ZnO/CPE can be successfully applied for the simultaneous determination of Pb\textsuperscript{2+} and Hg\textsuperscript{2+} in aqueous solution.

**Repeatibility, reproducibility, and stability of Co\textsubscript{3}O\textsubscript{4}-CeO\textsubscript{2}-ZnO/CPE**

In order to investigate the applicability of proposed electrode the repeatability, reproducibility and stability of Co\textsubscript{3}O\textsubscript{4}-CeO\textsubscript{2}-ZnO/CPE was tested in the optimum conditions. The proposed sensor showed excellent repeatability (n = 10) with an RSD\% of 2.2\% and 1.9\% for stripping peak currents of 1.0 nM Pb\textsuperscript{2+} and Hg\textsuperscript{2+}, respectively. The reproducibility of Co\textsubscript{3}O\textsubscript{4}-CeO\textsubscript{2}-ZnO/CPE was also investigated using preparation of ten electrochemical sensors in the same procedure. The RSD were calculated 2.9\% and 2.6\% for of 1.0 nM Pb\textsuperscript{2+} and 1.0 nM Hg\textsuperscript{2+} respectively. The stability of the proposed electrochemical sensor was investigated by detecting the SWASV responses of the electrode. The response of electrode for 1.0 nM of Pb\textsuperscript{2+} and Hg\textsuperscript{2+} retained 95.4 and 95.6\% of its initial stripping response after a period of 21 days. The results indicate that the Co\textsubscript{3}O\textsubscript{4}-CeO\textsubscript{2}-ZnO/CPE has excellent repeatability, reproducibility, and long-term stability.

**Analysis of spices sample**

Several tests were carried out in order to determination of Pb\textsuperscript{2+} and Hg\textsuperscript{2+} in different spices samples. As it can be seen in Table 3, the results of the measurements are comprised to those obtained by Atomic absorption spectroscopy (AAS) method which confirmed the accuracy and reliability of the method. Hence the proposed method can be used for individual and simultaneous detection of Pb\textsuperscript{2+} and Hg\textsuperscript{2+} in different spices samples. The results showed that the obtained data of proposed method are in good agreement with the reference method. Linear range and detection limit of the presented method was comprised with some recently reported methods (Table 4).

**Table 3 — Results for Pb\textsuperscript{2+} and Hg\textsuperscript{2+} determination (nM) in Spice samples under the optimum conditions**

<table>
<thead>
<tr>
<th>No.</th>
<th>Spice sample</th>
<th>Analyte</th>
<th>Found</th>
<th>AAS</th>
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<tr>
<td>1</td>
<td>Cinnamon</td>
<td>Pb\textsuperscript{2+}</td>
<td>154.1</td>
<td>158.9</td>
</tr>
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<td></td>
<td></td>
<td>Hg\textsuperscript{2+}</td>
<td>87.4</td>
<td>85.3</td>
</tr>
<tr>
<td>2</td>
<td>Hot pepper</td>
<td>Pb\textsuperscript{2+}</td>
<td>64.3</td>
<td>67.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hg\textsuperscript{2+}</td>
<td>53.1</td>
<td>55.9</td>
</tr>
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<td>3</td>
<td>Turmeric</td>
<td>Pb\textsuperscript{2+}</td>
<td>215.1</td>
<td>213.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hg\textsuperscript{2+}</td>
<td>42.5</td>
<td>39.4</td>
</tr>
<tr>
<td>4</td>
<td>Black pepper</td>
<td>Pb\textsuperscript{2+}</td>
<td>264.4</td>
<td>260.8</td>
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<td></td>
<td></td>
<td>Hg\textsuperscript{2+}</td>
<td>26.2</td>
<td>26.4</td>
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<td>5</td>
<td>Curry</td>
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<td>232.0</td>
<td>236.7</td>
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<tr>
<td></td>
<td></td>
<td>Hg\textsuperscript{2+}</td>
<td>86.2</td>
<td>85.3</td>
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<tr>
<td>6</td>
<td>Ginger</td>
<td>Pb\textsuperscript{2+}</td>
<td>151.2</td>
<td>156.0</td>
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<td>3.0</td>
<td>2.5</td>
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<tr>
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The comparison of the calibration curves of Pb\textsuperscript{2+} and Hg\textsuperscript{2+} in both individual or simultaneous determination shows that two analytes have no interfere with each other and the stripping current values are entirely similar at same concentrations. Hence, Co\textsubscript{3}O\textsubscript{4}-CeO\textsubscript{2}-ZnO/CPE can be successfully applied for the simultaneous determination of Pb\textsuperscript{2+} and Hg\textsuperscript{2+} in aqueous solution.

**Table 4 — Comparison of linear range and DL of the some recently suggested electrodes for the determination of Pb\textsuperscript{2+} and Hg\textsuperscript{2+}**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Linear range (nM)</th>
<th>DL (nM)</th>
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<td>Pb\textsuperscript{2+} Hg\textsuperscript{2+}</td>
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<td>PPh\textsubscript{3}/MWCNTs/IL/CPE</td>
<td>0.01–150.0</td>
<td>0.06</td>
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<td>IL/Gr/L/CPE</td>
<td>1.25–200.0</td>
<td>0.45</td>
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<tr>
<td>EDTA bonded conducting polymer modified electrode</td>
<td>0.75–100.0</td>
<td>0.60</td>
</tr>
<tr>
<td>Schiff base/MWCNT/CPE</td>
<td>0.75–100.0</td>
<td>0.45</td>
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<tr>
<td>[Ru(bpy)\textsubscript{3}]\textsuperscript{2+-GO modified Au electrode</td>
<td>50.0–250.0</td>
<td>1.41</td>
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<tr>
<td>Co\textsubscript{3}O\textsubscript{4}-CeO\textsubscript{2}-ZnO/CPE</td>
<td>0.27–18.42</td>
<td>0.054</td>
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</table>

The results show that the proposed method has excellent repeatability, reproducibility, and long-term stability.
Conclusions

This study provides a new modified carbon paste electrode based on Co$_3$O$_4$-CeO$_2$-ZnO tri-metallic nanocomposite for determination of Pb$^{2+}$ and Hg$^{2+}$ ions in aqueous solution and different kind of real samples. The obtained results suggest that Co$_3$O$_4$-CeO$_2$-ZnO nanocomposite is better than some other modifier of CPE for the electrochemical determination of heavy metals ions. The experimental results showed that the stripping peak currents were proportional to the concentration of Pb$^{2+}$ and Hg$^{2+}$ ions in the range of 0.27–18.42 and 0.42–31.30 nM with DLs of 0.054 and 0.097 nM, respectively. Hence, the proposed modified electrode can be used long term, providing a low detection limit (sub-nano molar), high selectivity, reproducibility, repeatability for determination of both analytes. The electrochemical sensor could also be renewed quickly and easily by mechanical polishing with a filter paper whenever needed. Consequently, the results showed the studied method would be a promising method to use in routine analytical applications.

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References