Article

A Simple, Cost-Effective Sensor for Detecting Lead Ions in Water Using Under-Potential Deposited Bismuth Sub-Layer with Differential Pulse Voltammetry (DPV)

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Abstract: The accumulation of high levels of lead or lead ions in a human body is harmful, particularly to children. Its neurotoxic effect is profound, damaging the central and peripheral nervous systems, resulting in stunted growth, behavioral problems and learning disabilities. The major source of lead or lead ions comes from the drinking water and tap water. The assessment of the water quality, including lead or lead ion content, is usually completed by a regional water department professional. This assessment is time-consuming and requires expensive instruments and skilled operators. Therefore, there is a need to produce a simple-use and relatively inexpensive method to detect lead or lead ions in water samples. This research has developed a simple-use, cost effective sensor system for the detection of lead ions in tap water. An under-potential deposited bismuth sub-layer on a thin gold film based electrochemical sensor was designed, manufactured and evaluated. Differential pulse voltammetry (DPV) measurement technique was employed in this detection. Tap water from the Cleveland, Ohio, USA regional water district was the test medium. Concentrations of lead ion in the range of 8 X 10^{-8} M to 8 x 10^{-4} M were evaluated. This DPV detection system required 3 -6 minutes to complete the detection measurement. A longer measurement time of 6 minutes was used for the lower lead ion concentration. The selectivity of this lead ion sensor was very good, and Fe III, Cu II, Ni II and Mg II at a concentration level of 5×10^{-4} M did not interfere with the lead ion measurement.

Keywords: under-potential deposition; bismuth sub-layer; lead ions; DPV

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1. Introduction

Lead is a highly poisonous metal, both to humans and the environment. Lead poisoning of children is a major environmental health problem. The neurotoxic effect of lead and lead ions is profound, damaging the central and peripheral nervous systems resulting in stunted growth, behavioral problems, and learning disabilities. A 10 μg/dL of lead ions in blood will affect the child's learning and behavior. A high lead level (≥70 μg/dL) can cause catastrophic health problems, including coma, seizures and even death [1]. Lead exposure to children ages 1-5 can affect nearly every organ system in the body with increasing risks in the damage of the brain and the nervous system, resulting in slow growth, learning behavior problems, as well as hearing and speaking deficiencies [1, 2]. Approximately half a million U.S. children under 5 years old have elevated lead levels (5 μg/dL) in blood [2-4]. The main exposure to lead or lead ions in humans comes from water sources. Therefore, effective protection of lead contamination is necessary, and the lead level should be able to be identified quantitatively and efficiently in both environmental and biological samples, including water sources [2-4].

The pollution of water sources by lead is devastating to human health. Currently, lead exists in metal water taps and interior water pipes. In addition, the corrosion of older water fixtures and solders result in lead leaching into the drinking water. Lead or lead ions are visible and can also be smelled or tasted by humans. However, the reliable method to assess lead or lead ion levels in water sources is to test the samples of the drinking water, tap water or water sources. This assessment is time –consuming, and it requires expensive analytical instruments and skilled operators. It is typically completed by water department professionals [2-4]. Therefore, a simpler and more efficient detection and measurement technology for lead ions in water will be of practical and scientific importance.

Currently, analytical methods for lead determination in water sources include flame atomic absorption spectrometry (FAAS), electro-thermal atomic adsorption spectrometry (ET-AAS), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectrometry (ICP-OES) and others. These techniques can provide accurate information about the levels of lead ion in the water sample. However, the analytical methods are elaborate and require expensive instrumentation [5-8].

In this study, a simple–use, cost-effective sensor system for the detection of lead ions in water was developed. This lead ion detection sensor used a thin gold film based electrochemical sensor with a thin layer of bismuth. The bismuth layer was deposited on the gold film based electrode elements by under-potential deposition technique. Under-potential deposition provided monolayer or sub-layer of the bismuth on the gold electrode elements enhancing the sensitivity of detecting lead ions by the bismuth film. Subsequently, the overall sensitivity of the sensor increased. Differential pulse voltammetry (DPV) was the transduction mechanism used for this sensor system. Tap water from the Cleveland, Ohio, USA regional water district was used as the test medium. Lead ion concentrations of 5×10^{-4} M to 8×10^{-7} M in tap water were tested. Potential interference studies by other metal ions including iron III, copper II, nickel II and magnesium II at the concentration level of 5×10^{-4} M were carried out, demonstrating that our developed sensor processed excellent selectivity without interference by any of these metallic ions. Characterization of the bismuth was performed using Time-of-Flight secondary ion mass spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS). Our study showed that the total detection time for lead ions in the water was within 3 minutes at a lead ion concentration level of 10^{-4} M or above, and by using 6 minutes for lower lead ions concentration at 10^{-7} M. This operation time could be further optimized. Furthermore, the cost of fabricating and developing this single-use sensor for lead detection was estimated to be less than $2 US dollars. Thus, a simple use, cost effective practical sensor for lead ion detection in water became a true reality.

2. Materials and Methods

2.1. Apparatus and Reagents

Bismuth (III) nitrate pentahydrate (Cat. # 383074) and lead (II) nitrate (Cat. # 228621) were obtained from Sigma-Aldrich (St. Louis, MO). Iron (III) sulfate pentahydrate (Cat. #AC345231000), nickel (II) sulfate hexahydrate (Cat. # N73-100), copper (II) sulfate pentahydrate (Cat. # BP346), magnesium (II) sulfate heptahydrate (Cat. # M63), sodium chloride (Cat. # S271), potassium hydroxide pellets (Cat. #P1767), concentrated H_2SO_4 95.0 to 98.0 w/w % (Cat. # A300) and concentrated HNO_3 70% w/w % (Cat. # A200) were received from Fisher Scientific (Pittsburgh, PA.). A CHI 660C (CH Instrument, Inc., Austin, TX) Electrochemical Workstation was used for DPV and EIS investigations. Similar Model CHI 660 A-E Electrochemical Workstations could also be used. All the experiments were conducted at room temperature. Characterization of the bismuth film was performed using a PHI TRIFT V nanoTOF Time-of-Flight Secondary Ion Mass Spectrometer (TOF-SIMS) and a PHI Versaprobe 5000 Scanning X-Ray Photoelectron Spectrometer (XPS).

2.2 Design and Fabrication of the Sensor

This basic sensor involved a platform designed in our laboratory. It consisted of a three-electrode electrochemical configuration sensor system. Both working and counter electrodes were thin gold film of 50 nm in thickness. The thin gold film was deposited by sputtering technique on a roll-to-roll manufacturing basis. The reference electrode was a thick-film printed Ag/AgCl electrode. Laser ablation technique was used to define the size and structure of the electrode elements and the overall sensor structure. This manufacturing process employed known micro-fabrication procedures, such as sputtering physical vapor deposition, laser ablation and thick film printing techniques, resulting in a high-reproducible and low-cost single-use disposable sensor which was very beneficial for simple-use, disposable, cost effective *in situ* applications. The overall dimensions of an individual lead ion detection sensor were 33.0 x 8.0 mm^2. The working electrode area was 1.54 mm^2 accommodating 10-25 μL of liquid test sample. Details of the design and fabrication of this platform thin gold-film based sensor were given elsewhere [10, 11].

2.3. Modification and Preparation of the Lead Ions Sensor

2.3.1. Chemical Pretreatment of the Thin Gold Film Electrode Elements

A 3-step chemical pretreatment procedure was applied to the sensor in order to eliminate the oxidized compounds and any other residue from the gold film electrode element surface. The purpose of pretreatment was to minimize the electrode charge transfer resistance, thereby improving the sensitivity and the reproducibility of the sensor. This pretreatment procedure was based on other reported investigation [9, 10] as well as in our own previous studies [11, 12]. Typically, a batch of 8 thin gold film based sensors were immersed in a 2M KOH solution for 15min. After rinsing with copious amounts of DI water for about 30 seconds, the sensors were placed in a 0.05 M H_2SO_4 solution (95.0 to 98.0 w/w %) for another 15 min. DI water was then used to rinse the sensor prototypes for another 30 seconds. The sensors were then placed in a 0.05 M HNO_3 solution (70% w/w %) for another 15 minutes. The sensors were rinsed one more time with DI water for 30 seconds and dried gently in a steam of nitrogen. The EIS study of this pretreated sensor showed excellent reproducibility as reported in our other studies. [11, 12]

2.3.2. Under-Potential Deposition of Bismuth on the Thin Gold Film Based Sensor

Bismuth was considered unique for lead ion detection. Thus, bismuth-modified electrochemical based electrodes were proposed for lead ion detection in different test media [6, 13-18]. One advantage of using bismuth film for the detection of lead ions was that the dissolved oxygen in the test medium did not interfere with the measurement of lead ion [19-21]. Thus, the use of bismuth to detect lead ions would not require removing the dissolved oxygen in the test medium which was very attractive for practical applications. Thus, bismuth film was adopted to be used in this lead ion detection approach. However, the limited sensitivity and specific test medium required condition (alkaline solution) of using a bismuth film for lead ion detection limited its practical applications of the lead ions detection in a water medium.

Under-potential deposition was a known electrochemical process. In this deposition process, the sub-layer of the selected metallic deposition was known to be extremely sensitive to the surface structure of the electrode, enhancing the sensitivity of electrode *per se* [22-24]. Our previous investigation of under-potential deposited metallic films in sub-layer thickness demonstrated the enhancement of the sensitivity of the sensor itself also, such as cadmium and thallium sub-layers for the detection of carbon dioxide and glucose, respectively [25, 26]. Thus, a unique aspect of this study was that an under-potential deposited bismuth film on the thin gold film based sensor was first prepared for the lead ion detection sensor, providing the sensitivity for this lead ion detection. The under-potential deposition of bismuth might be monolayer or sub-layer. Assessment of the actual monolayer or sub-layer of bismuth film is beyond the scope of this research and will not be discussed in this study. For practical application, the under-potential deposited bismuth sub-layer provided the sensitivity of the lead ion detection sensor was our motivation in this study. In a typical preparation of this step, cyclic voltammetry was first applied for the bismuth film deposition. A bismuth ion solution was prepared. 0.025M of Bismuth (III) nitrate pentahydrate was mixed in 1M of nitric acid with 1mM of sodium chloride solution. A full range of CV scan for bismuth deposition was then conducted, assessing the reduction potential for bismuth onto the gold electrode. A similar

CV deposition of bismuth on gold was also conducted by Hara et al [24]. Cathodic potentials were observed with different thicknesses of bismuth layer on the surface. For our CV study, the reduction potential of bismuth was set at -0.25V versus the thick-film printed Ag/AgCl reference electrode as shown in Figure 1. In a typical experience, 20 µL of prepared bismuth solution was placed on the sensor and a potential sweep from -0.50V to -0.40V of the cyclic voltammetry was used for the under-potential deposition of the bismuth on the gold electrode. After deposition, the bismuth sensor was rinsed with deionized water for 10 seconds and dried gently by nitrogen. This preparation step of this under –potential deposition of bismuth film could be accomplished prior to the actual water sample testing. Figure 1 shows the typical CV used for this under-potential deposited bismuth film. Bismuth layer was visible and prepared sensors could then be stored at 4 °C, ready for use.

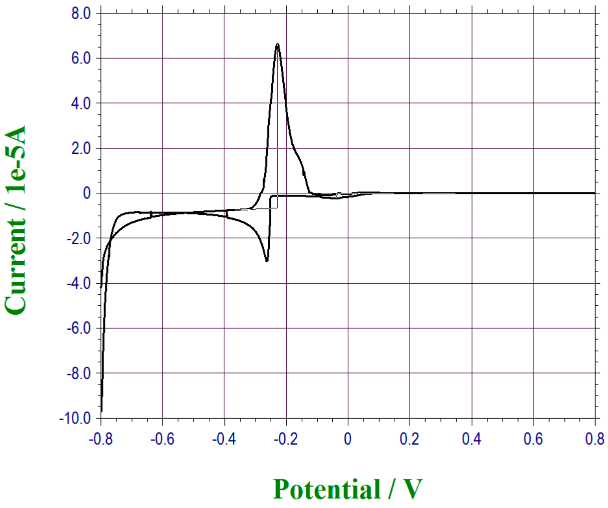

Figure 1. Cyclic voltammetry for the full range of scanning for bismuth reaction potential.

2.3.3. TOF-SIMS and XPS Analysis for the Bismuth Sublayer

2.3.4. Surface characterization of Bismuth Sublayer with XPS and TofSIMS

The bismuth sub-layer formed by the under-potential deposition described above was examined using X-ray photoelectron spectroscopy and Time-of-Flight secondary ion mass spectrometry (TOF-SIMS). PHI Versaprobe 5000 Scanning X-Ray Photoelectron Spectrometer (XPS) and PHI TRIFT V nanoTOF Time-of-Flight Secondary Ion Mass Spectrometer (TOF-SIMS) were employed. In this characterization study, two different bismuth concentrations were used, sample A (0.1M) and sample B (0.25 M) of bismuth nitric solutions

Figure 2 and 3 and Table 1 show the XPS analysis of the bismuth film deposited, quantifying the bismuth film composition acquired with a monochromated aluminum K alpha X-ray with an energy of 1486.7 eV and a spot size of 200 µm. The spectrum was acquired with a 90 degree take off angle to increase the surface sensitivity. The survey scan was acquired with a Band pass of 93.9 eV. An average of 8 rounds of acquisition on a range of 0 to 1100 eV was scanned every 0.4 eV for 25ms.

Figures 2 and 3 show the bismuth sublayer was successfully deposited by the under-potential deposition technique. As expected and demonstrated in Figure 3, the 0.25 M of bismuth nitric solution provided a better coverage of the gold film based sensor. Therefore, 0.25 M of bismuth nitric solution was used throughout this investigation. Table 1 shows the XPS results of the atomic percentage of the samples A and B with the higher bismuth atomic percentage in sample B.

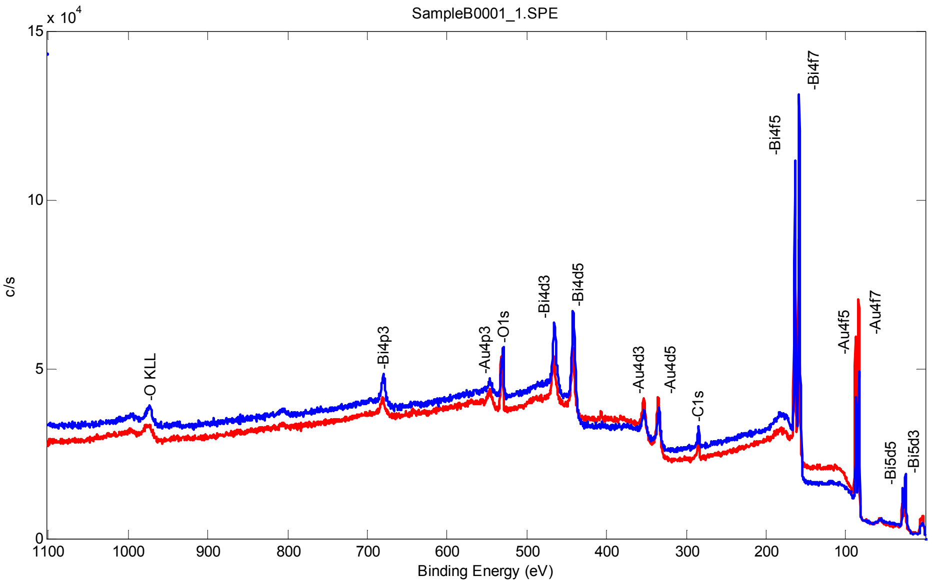

Figure 2. Survey scan from XPS measurements at 90 degrees take of angle comparing samples A (red) and B (blue)

Table 1. Concentration of different elements [in Atomic Percent] compared for samples A and B

	C1s	**O1s**	**Au4f**	**Bi4f**
Sample A	31.1	40.7	15.2	13.0
Sample B	27.5	40.5	10.3	21.8

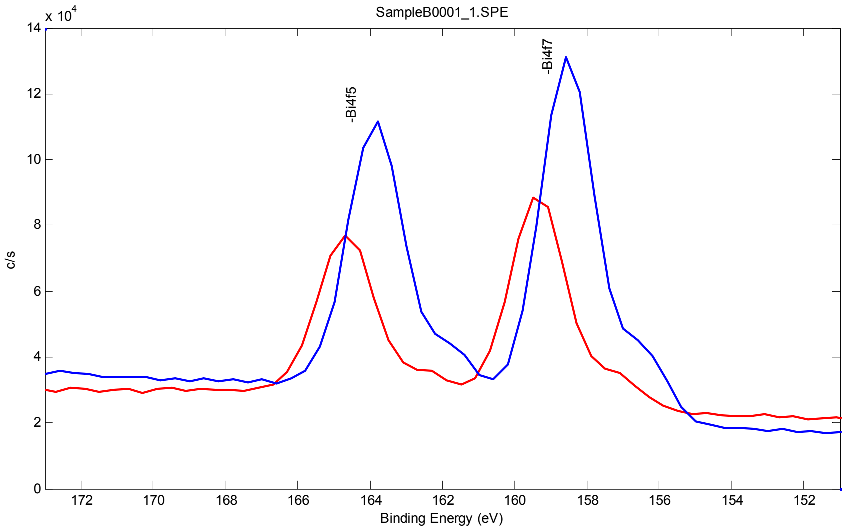

Figure3. Bismuth 4d 7/2 peak from the Survey spectrum compared for samples A (red) and B (blue)

TofSIMS measurements were performed in the negative polarity. At this negative polarity, bismuth and gold provided good information with a primary source of Ga. Experimentally, the primary source was a Ga^+ beam accelerated to 30KV and bunched to a pulse size of 7ns and an acquisition rate of 22KHz. Using this setting, the surface of the electrode could be mapped with a spatial resolution of 500 nm. Map stitching was then used to generate ion maps with a total area of 2 mm x 2mm.

Figure 4 shows the TOF-SIMS analysis of the under-potential deposited bismuth structure on the gold film based sensor. Figure 4(a) shows the gold film based working electrode element of sensor, and Figure 4(b) shows the bismuth film deposited on the gold based working electrode element using a 0.25 M bismuth nitric solution and at an electrochemical potential range of -0.45V- -0.35 vs a Ag/AgCl thick film printed reference electrode.

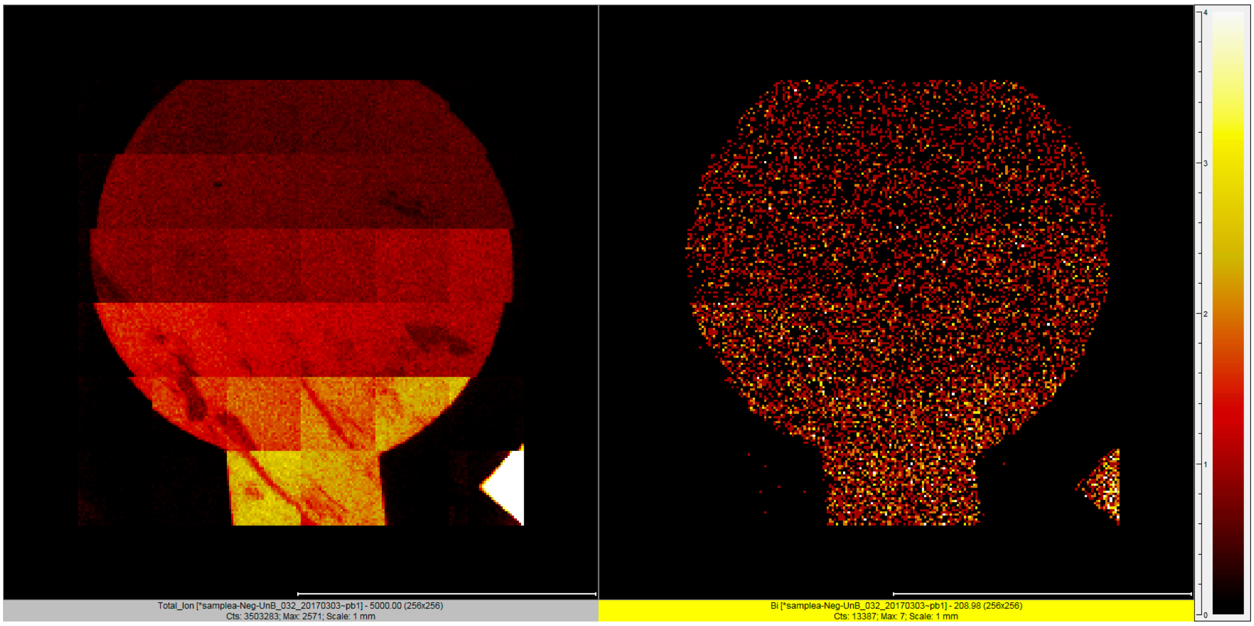

Figure4. The total secondary ions acquired at the negative polarity of gold (on the left) and the bismuth ion image (on the right) using a Ga^+ primary source.

The homogeneity of the bismuth film was evident. The compositions of the bismuth film deposited was mainly bismuth, as expected. Also as expected, the bismuth film deposited with the concentration of 0.25 M bismuth nitric solution was higher than that with 0.1 M bismuth nitric solution (data did not included).

3. Results and Discussion

3.1 Anodic Stripping of Lead Ions by Differential Pulse Voltammetry (DPV)

The under-potential deposited bismuth sub-layer on the thin gold film sensor as described in Section 2.3.2, was ready for lead ion detection**.** Anodic stripping of the lead ions from the bismuth sub-layer produced a current output which was used to quantify the lead ions in the test medium. Differential pulse voltammetry (DPV) was employed as the transduction mechanism of this sensor system. Differential pulse voltammetry (DPV) applied a linear sweep voltammetry with a series of regular voltage pulses superimposed on the linear potential sweep [27, 28]. Consequently, the current is measured immediately before each potential change. Thus, the effect of the charging current is minimized, achieving a higher sensitivity. DPV was employed in this lead ion detection.

3.2 Deposition of Lead Ions on the Bismuth Sub-layer

Lead ions deposited on the bismuth sub-layer was a time-dependent. The lead ions in the test medium reduced forming Pb(Bi) complex on the bismuth sub-layer [20,21, 29,30]. The DPV measurement of the anodic stripping current of the lead ions was then used to quantify the lead ions in the test medium. As expected, the longer the time that allowed the lead ions to be attached to the bismuth sub-layer, the higher the anodic stripping current measured by DPV resulted. In this phase study, 8×10^{-4} M lead ions in the tap water was used as the test medium. The period of time (the retention time) for the lead ions deposited on the bismuth sub-layer varied between 10 to 120 seconds. Typically, 20µL of the test water sample was placed on top of the sensor surface. After the retention time, DPV measurement was then carried out. As expected, the highest anodic stripping current was obtained at 120 seconds, and the anodic stripping current was decreased in sequential order of 90, 60 and 10 seconds. Thus, 120 retention time was used in our detection of lead ions in tap water at this lead ion concentration level. The DPV measurement was completed in 60 seconds. Therefore, the overall time required for the detection of this lead ion level was within 3 minutes. This operating time has not been optimized and could be further modified. Figure 5 shows the results of this study.

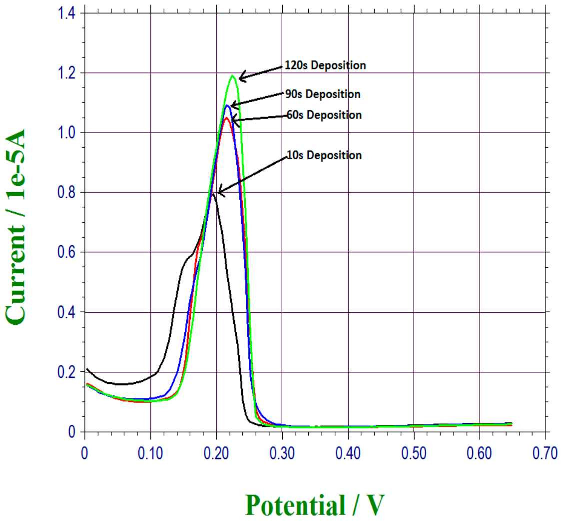

Figure 5. Electrochemical stripping analysis of lead ions for different deposition time ranging from 10s to 120s.

Consequently, a fixed retention, 120 seconds in this case, would be used for the practical application of the lead ion detection sensor system.

3.3 Detection of Lead Ions in Tap Water

Normal tap water from the Cleveland regional water district, Cleveland, OH. USA, was used as the test medium for this lead ion sensor detection. Lead (II) nitrate in proper quantity was added into the tap water preparing for the lead ions contained tap water test sample. In a typical experiment, 20 μL of the test water sample was placed on top of an under-potential deposited bismuth sub-layer thin gold film based sensor. At this 10^{-4} M lead ions concentration, a retention time period of 120 seconds was used based on the results described in Section 3.2. After this retention time, DPV measurement of the anodic stripping current was then undertaken. Figure 6(a) shows the DPV measurement of four lead ions concentrations in the tap water, namely, 5×10^{-4} M, 2.5×10^{-4} M, 1×10^{-4} M, and 0.25×10^{-4} M with n>3. Figure 6(b) shows the calibration curve based on the DPV measurements obtained in Figure 6(a). The least square fit of this calibration curve is Y=1.16X-0.02 with R^2 value of 0.970. The results of this test demonstrated that the accuracy of detecting lead ions in tap water using this under-potential deposited bismuth sublayer thin gold film based electrochemical sensor with DPV measurement was very good. The retention time was 120 seconds and the DPV measurement time was 60 seconds. Thus, the total time for the detection of lead ions could be accomplished within 180 seconds (3 minutes).

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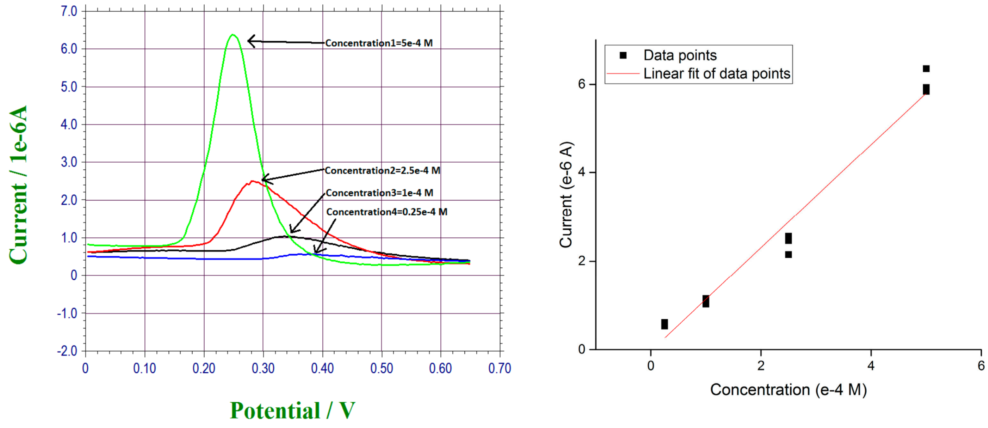

(a) (b)

Figure 6. a) DPV measurement of lead ions concentration level ranging from 5×10^{-4} M to 2.5×10^{-5} M. b) Calibration curve for the DPV measurement data points.

Lower lead ion concentrations could be detected using this under-potential deposited bismuth sub-layer on this thin gold film based sensor and with DPV measurement. As suggested in Section 3.2, the rate at which lead ions adhered to the bismuth sub-layer was a time-dependent function. . Experimentally, tap water sample containing a low level of lead ions (20 μL) was placed on top of the sensor identical to the process described above. However, at this lower lead ions concentration level, the retention time was set at 300 seconds (5 minutes), and DPV measurement was then carried out. It also required 60 seconds to complete the DPV measurement. Figure 7 shows the DPV measurement of lead ions in tap water with a lead ion concentrations of 1.6×10^{-6} M and 8×10^{-7} M. It was apparent that this under-potential deposited bismuth sub-layer on thin gold film sensor was capable of detecting lead ions in tap water as low as 8×10^{-7} M. The detection process required a total of 360 seconds (6 minutes) using the DPV measurement technique.

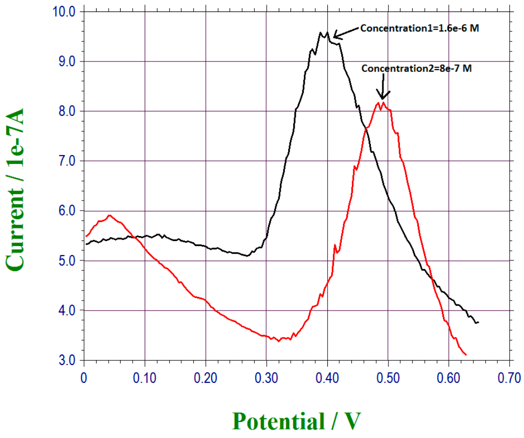

Figure 7. DPV measurement of lead concentration levels of 1.6×10^{-6} M and 8×10^{-7} M.

Based on the results shown in Figures 6 and 7, a retention time of 300 seconds would cover the lead ions concentration range of 8×10^{-7} M to 5×10^{-4} M. The retention time needed for the lead ions detection can be further optimized.

3.4. Interference Study of This Lead Ions Sensor

Selectivity is very important for the development of a sensor. This suggested that the operation of the sensor should not be interfered with other chemicals that might be presented in the test medium. Fe III, Cu II, Ni II and MG II and were considered to be carcinogens and may also interfere with lead bismuth reaction [31-34]. Iron sulfate pentahydrate, cooper sulfate pentahydrate, nickel sulfate hexahydrate and magnesium sulfate heptahydrate were used. Each of these chemicals was used to prepare a 5×10^{-4} M concentration test sample with the Cleveland regional water district tap water. Similar to the test procedure described above, 20 µL of the water sample was placed on top of a prepared lead ion sensor. The retention time was set at 300 seconds ensuring that the metal ions were anodic stripped from the bismuth sub-layer. DPV measurement was undertaken after the retention time 300 seconds. Similar to our standard test, the DPV measurement took 60 seconds. Figure 8 shows that none of the Fe III, Cu II, Ni II and Mg II at 5×10^{-4} M in tap water contribute to the DPV measured current of 5×10^{-4} M lead ions in the tap water sample. This result indicated the excellent selectivity of the under-potential deposited bismuth sub-layers of a thin gold film based sensor for lead ion detection.

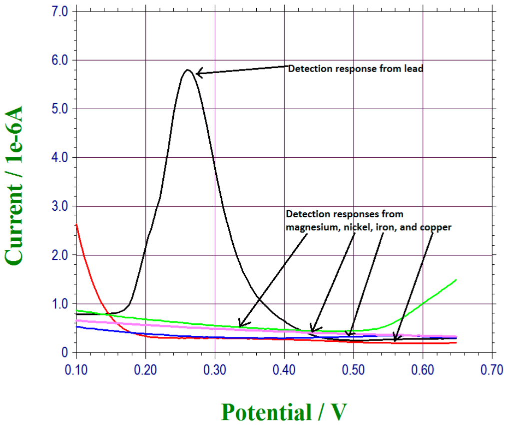

Figure 8. Interference test for the bismuth sensor.

4. Conclusion

A unique lead ion detection sensor system was successful developed. This sensor used an under-potential deposited bismuth sub-layer on a thin gold based electrochemical sensor. Differential pulse voltammetry (DPV) was the transduction mechanism employed in this detection system. Lead ions in normal tap water from the Cleveland regional water district was used as the test medium. Lead ion concentrations of 0.24×10^{-4} M to 8×10^{-7} M were detected within 3-6 minutes including the retention and DPV measuring times. Fe III, Cu II, Ni II and MG II at 5×10^{-4} M concentration in tap water samples did not contribute to the DPV current output of lead ions detection,indicating the sensor was highly selective to lead ions without other interference.

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Author Contributions: C.C.L. and Y.D. conceived and designed the experiments; Y.D. performed the experiments; C.C.L., and Y.D. analyzed the data; Y.D., and C.C. L. contributed to prepare this manuscript.

Conflicts of Interest: The authors confirm that this article content has no conflict of interest.

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