Electrochemical Detection of Trichloroethylene with an Electrodeposited Pb-Modified Electrode

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The amperometric sensing of trichloroethylene (TCE) in the organic phase by using modified Pb electrode was described. The influence of pretreatment, electrodeposition current density, electrodeposition time, and electrodeposition temperature for preparation of the working electrode were discussed. The optimal conditions for preparation of modified Pb electrode were obtained as 0.1 M HNO₃ pretreatment, 20 mA/cm² electrodeposition current density, and 30°C electrodeposition temperature. Additionally, the optimal sensing conditions such as ~2.10 V sensing potential [vs. Ag/Ag⁺] with 0.1 M tetrabutylammonium perchlorate in acetonitrile (AN) solution; 155 ppm agitation rate, and at room temperature with 0.01 M tetrabutylammonium tetrafluoroborate electrolyte concentration in AN solution were obtained in this system. Under the optimal sensing conditions, the results indicated that the response time was 20 s (90% response time) and the correlation of sensing response current, iₜ, and TCE concentration, Cₜ, is iₜ = 1.060 Cₜ in the range from 100 to 700 ppm. Furthermore, the rate constant of TCE mass transfer, k, was also obtained to be 7.217 × 10⁻⁴ cm s⁻¹.


Trichloroethylene (TCE) is a generally used chemical material in industries such as electronic manufacturing, plastics production, textile process and organic synthesis. At the same time, TCE is also an organic chemical that has been used in dry cleaning, for metal degreasing, and as a solvent for oils and resins. Besides, the waste solution is also a contaminant in the soil or groundwater around environment. Furthermore, TCE was confirmed to be a carcinogenic material in many medical investigations. Therefore, to detect and monitor TCE concentration in order to protect people health is very important in the working environment.

At present, the monitoring of TCE relies principally on gas chromatography, which provides good sensitivity and selectivity. However, this method is not well suited for use as a simple, portable measuring devices. Besides, other analytical techniques such as electrochemical method, spectroscopic method, photocalytic oxidation method, and biochemical method have been applied to detect the concentration of TCE. All these methods had some disadvantages, for example, complicated operation, high cost, poor stability, and long measurement time. Furthermore, all these mentioned analytical instruments cannot, minimization in production and in situ, apply in the field for automatic monitoring of TCE concentration.

Sensors may be the most practical monitor setup because of their convenience, accuracy, easy minimization, and automation-in situ measurement. Several TCE sensors have been developed such as fiber-optic-based TCE sensor, and flow injection TCE sensor. However, these sensors may have some disadvantages also, for example, unstable, expensive and long response time. Therefore, it is necessary to develop a new TCE sensor with good performance, simple structure, and lower cost.

In this work, an electrodeposited Pb-modified electrode was used to sense TCE because this configuration has been shown to give good performances, simple structure, and lower cost. Therefore, it is necessary to develop a new TCE sensor with good performance, simple structure, and lower cost.

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Experimental

Chemicals and instrumentation.—The electrodeposition solution components of Pb were purchased from several sources: lead(II) tetrafluorooborate [Pb(BF₄)₂, Alfa Aesar, USA], tetrfluorooboric acid (HBF₄, Riede-de Haen, Germany), boric acid (H₃BO₃, Alfa Aesar, USA), and polyethylene glycol (PEG 300, Hayashi, Japan). The tetrabutylammonium tetrfluoroborate (TBAT) and tetrabutylammonium perchlorate (TBAP) are all GC grades of TCI (Japan). The acetonitrile (AN) and TCE are high performance liquid chromatography and gas chromatography grades of Tedia (USA) and Aldrich (USA), respectively. All aqueous solutions were prepared with deionized (DI) water purified to a resistivity of at least 18.3 MΩ cm by a water purification system (Milli-RO 60, Japan). Additionally, the surface structure of the prepared electrode was characterized with scanning electron microscopy (SEM, FE-S 4200, Hitachi, Japan), X-ray diffraction (XRD, D/max 3. V, Rigaku, Japan), and electron spectroscopy for chemical analysis (ESCA, VG/ESCA 210, U.K.).

Preparation of working electrode.—The Pb foil (6 × 1 × 0.01 cm, Alfa Aesar, USA) attached to an alumina plate (5 × 1.5 × 0.1 cm, Lei Ke, Taiwan), then the sensing area 1 cm² was controlled by Teflon tape. The working electrode was ultrasonically cleaned in 0.1 M HNO₃ aqueous solution, then washing with DI water thoroughly. After, the Pb foil substrate was immersed in electrodeposited Pb aqueous solution containing 0.63 M Pb(BF₄)₂, 0.68 M HBF₄, 0.43 M H₃BO₃, and 0.0006 M PEG 300. Then, the electrodeposition of Pb for preparation of the working electrode was carried out at 30 rpm agitation rate. Electrodeposition current density, time, and temperature were adjusted, respectively, to control the electrodeposition process.

Sensing procedures.—All electrochemical measurements were carried out in a conventional three-electrode electrochemical cell with a 263A electrochemical analysis system (EGA/G, USA). The modified Pb electrode was used as working electrode. A platinum plate and Ag/Ag⁺ (with 0.1 M TBAP in AN solution) were used as auxiliary and reference electrodes, respectively. After, the sensing potential was set in the limiting current region. Then, the steady state amperometric signals were obtained, i.e., the background current. Immediately, a desired concentration of TCE was added into the sensing system, then the amperometric current of the working electrode was also attained, i.e., the measured current. The response current is equal to the measured current minus the background current.

Analysis and identification of products.—The GC-mass analysis was performed on a Hewlett-Packard 5890 gas chromatograph (GC) connected to an ion trap detector, for separating the volatile material and then into a VG 70–250S mass spectrometer. The GC was equipped with a 30 m Rtx-5 capillary column. The column temperature was held at an initial temperature of 100°C for 2 min and then increased at 6°C/min to 190°C where it was held for 20 min. High
purity helium (99.99%) was used as carrier gas at a flow rate of 36 mL/min. Electron impact mass spectroscopy was used at the ionization energy of 70 eV.

Results and Discussion

Surface morphology of the electrode.—Comparison of the pretreatment time on the electrode surface morphologies is shown in Fig. 1. In Fig. 1A, the electrode without treatment by a 0.1 M HNO\textsubscript{3} aqueous solution, the smooth surface of electrode was obtained. On the other hand, in the Fig. 1B, the Pb electrode with treatment by a 0.1 M HNO\textsubscript{3} aqueous solution, the electrode surface showed large roughness more than that without treatment by a 0.1 M HNO\textsubscript{3} aqueous solution. These data clearly indicated that increasing the size of the voids increased the amount of deposited Pb. Consequently, the 1 h pretreatment by a 0.1 M HNO\textsubscript{3} aqueous solution was chosen as the pretreatment condition for preparation of the working electrode.

Determination of the amperometric potential window.—The current/potential curves at different concentrations of TCE by using electrodeposited Pb-modified electrode were shown in Fig. 2A. The results show that increasing the concentration of TCE from 0 to 500 ppm, increased the measured current for TCE reduction. This is understandable, because in the electrochemical reaction, the reduction current increased with the increase of the TCE concentration.

Moreover, the limiting current region at the concentration of 500 ppm TCE was shown in Fig. 2B. In Fig. 2B, the response current is equal to the measured current (500 ppm) minus the background current (0 ppm TCE). The result showed that increasing the driving force from $-1.98$ to $-2.06$ V (vs. Ag/Ag\textsuperscript{+} with 0.1 M TBAP in AN solution) increased the current of reduction. The result showed that the response current was controlled by both kinetic and mass-transfer mechanisms in this potential range. Further increasing the potential from $-2.06$ to $-2.14$ V (vs. Ag/Ag\textsuperscript{+} with 0.1 M TBAP in AN solution), the current reached a constant, thus the reaction was only controlled by mass transfer in that potential range. And then, the current rapidly increased when the potential increased from $-2.14$ to $-2.28$ V (vs. Ag/Ag\textsuperscript{+} with 0.1 M TBAP in AN solution); the response current increased due to the decomposition of electrolyte. In Fig. 2B, the main reduction of TCE took place between the potential from $-2.06$ to $-2.14$ V (vs. Ag/Ag\textsuperscript{+} with 0.1 M in AN solution).
Because $-2.10 \text{ V} \text{(vs. Ag/Ag}^+\text{ with 0.1 TBAP in AN solution)}$ is within this constant current region, its sensing reaction is mass-transfer controlled. Conclusively, the reasonable and suitable applied potential for TCE sensing in this system was chosen to be $-2.10 \text{ V} \text{(vs. Ag/Ag}^+\text{ with 0.1 TBAP in AN solution)}$.

**Effect of pretreatment time with 0.1 M HNO$_3$**—Effect of pretreatment time with 0.1 M HNO$_3$ aqueous solution on the sensitivity is shown in Fig. 3. The result shows that increasing the pretreatment time with 0.1 M HNO$_3$ aqueous solution from 0 to 60 min, increased the sensitivity from 0.28 to 1.06 $\mu$A/cm$^2$ ppm. Apparently, the untreated Pb foil by 0.1 M HNO$_3$ aqueous solution exhibited bad performance for TCE sensing. It can be explained that the void fraction and coarseness increased with pretreatment time in the 0.1 M HNO$_3$ aqueous solution. Consequently, the optimal pretreating condition is 60 min pretreatment time.

**Effect of electrodeposition current density**—Effect of electrodeposition current density on the sensitivity for sensing of TCE is shown in Fig. 4. The result shows that increasing the electrodeposition current density from 0 $\text{mA/cm}^2$ i.e., original Pb foil to 20 mA/cm$^2$ for preparing the modified Pb electrode, decreases the sensing sensitivity from 1.813 to 1.060 mA/cm$^2$ ppm. The surface morphologies of modified Pb electrode at different electrodeposition current densities for preparing the modified Pb electrode are shown in Fig. 5. These data clearly suggest that the working electrode surface was not electroplated completely under 5 and 10 mA/cm$^2$ electrodeposition current densities, respectively, which induced the different sensitivity.
TCE by using these electrodes. However, the unstable and nonlinear response current was apparently found during the sensing reaction when the electrodeposition current density for preparing the working electrode was smaller than 20 mA/cm² as shown in Fig. 6. It may have been due to the formation of unstable material with negatively charged metal particles on the Pb electrode surface which induced the failure of the sensing reaction. Additionally, the XRD patterns and ESCA spectra of naked and electrodeposited Pb electrodes are shown in Fig. 7 and Table I, respectively. Comparison of the data of Fig. 7A and B clearly suggest that the crystal structure was transformed from a face centered cubic structure to a tetragonal structure between the general Pb metal and the electrodeposited Pb. Additionally, comparison of Tables IA and B show that the B, F elements were only indwelled on the surface of electrodeposited Pb-modified electrode. Consequently, the 20 mA/cm² electrodeposition current density for preparing the working electrode was chosen for further development of the TCE sensor.

**Effect of electrodeposition time.**—The sensitivity of the sensing of TCE was investigated as a function of electrodeposition time for preparing the modified Pb electrode as shown in Fig. 8. The result indicated that increasing the electrodeposition time from 1 to 2 h deceased the sensing sensitivity of TCE from 1.910 to 1.060 mA/cm² ppm. Then, the sensitivity increased slightly from 1.060 to 1.280 mA/cm² ppm when the electrodeposition time increased from 2 to 4 h. However, an unstable and nonlinear response current was obtained also, when the electrodeposition time for preparing the working electrode was 1 h. Additionally, Fig. 8 clearly suggests that the Pb film thickness and deposition time are insignificant factors on the sensitivity of the TCE sensor. Comparing the energy consumption and small enlargement effect of sensitivity, the 2 h electrodeposition time was chosen to prepare the working electrode.

**Effect of electrodeposition temperature.**—The effect of temperature for preparing the electrode on the sensitivity of the TCE sensor was shown in Fig. 9. The result shows that increasing the electrodeposition temperature slightly increased the sensitivity. For example, increasing the electrodeposition temperature for preparing the working electrode from 25 to 40°C slightly increased the sensitivity of TCE sensing from 0.854 to 1.210 µA/cm² ppm. The active
surface area increased slightly by SEM morphology with increasing temperature results in an insignificant increase of sensitivity. However, the electrodeposition temperature for preparing the electrode showed a positive effect on the sensitivity. However, in this system, the temperature was over 40°C which allowed the formation of hydrofluoric acid as shown in Eq. 1:

\[
4\text{HF} + \text{H}_3\text{BO}_3 \rightarrow \text{HBF}_4 + 3\text{H}_2\text{O}
\]  

(1)

In order to prevent the vent of HF gas, the 30°C electrodeposition temperature was chosen as temperature for preparing the electrode.

Amperometric measurement of TCE.—Under previously selected optimal conditions for preparation of working electrode, the typical amperometric response curves at single and different TCE addition concentration for detection of TCE by using an electrodeposited Pb-modified electrode are shown in Fig. 10. Curve A of Fig. 10 shows that one 100 ppm concentration of TCE was injected into the electrochemical cell for each sensing step, and that the response current increased rapidly and reached a steady state. Additionally, curve B was obtained by different injection concentration of each sensing step. Comparison of the curves A and B in Fig. 10 shows that a similar amperometric response current curve and identical sensitivity were obtained. These data clearly show that TCE sensing has good reliability on the sensitivity and reproducibility. Additionally, response currents are plotted against the TCE concentration resulting in a straight line in the range from 100 to 700 ppm of TCE concentrations as shown in Fig. 11. The equation of linear fitting is \(i = 1.060[T\text{CE}] + 9.167\), where the slope of the straight line is 1.060 μA/cm² ppm which is the sensing sensitivity and the \(R^2\) is over 0.998.

Reaction mechanism.—Figure 12 shows that the peak for gas chromatography-mass spectroscopy of the main product locates at 60 of molecular weight. Hence, the product of electrolysis was acetylene chloride. Furthermore, after electrolysis, an AgNO₃
aqueous solution was added to the catholyte and the white AgCl was found. It can be confirmed that chlorine ion presents in the catholyte. Moreover, the pH of catholyte decreased from 7.0 to 1.0 during the electrolysis. All results show that hydrogen ion is generated in the catholyte after electrolysis. The acetylene chloride not only has stronger acidity than TCE but also dissociated to acetylene chloride anion in the solution. The electrochemical reduction mechanism for TCE by using electrodeposited Pb-modified electrode as working electrode is proposed as shown in Eq. 2.

\[
\text{CHCl} = \text{CCl}_3 + \text{H} \rightarrow \text{H} + 2 \text{Cl}^- + \text{CCl}_3
\]

**Comparison of the experimental results and the theoretical ones.**—The sensing reaction was mass-transfer controlled and the TCE concentration was less than 700 ppm, the relationship of diffusion current, \(i_d\), and the concentration of TCE in the solution, \(C_L\), can be described as shown in Eq. 3.

\[
i_d = ZF a k C_L
\]

where \(Z\) is the number of electron transfer, \(F\) is the Faraday constant, \(A\) is the sensing area of electrode, and \(k\) is the rate constant of mass transfer control. Equation 3 implies a linear relationship between TCE concentration and cathodic current. The relationship of \(i_d\) and \(C_L\) at the desired sensing conditions was obtained from the data of Fig. 11 resulting in Eq. 4.

\[
i_d = 1.060 C_L
\]

Comparing Eq. 3 and 4 and substituting the number of electron transfer, \(Z\) which is 2, \(26\) and \(A\) which is 1.0 cm\(^2\), \(k\) can be obtained to be 7.217 × 10\(^{-4}\) cm\(^2\) s\(^{-1}\).

**Conclusions**

Electrodeposition of Pb has been shown to be a suitable metal catalyst as sensing electrode for amperometric TCE sensor. The SEM morphologies of prepared working electrode show that the substrate surface has the larger roughness by pretreating electrode with 0.1 M HNO\(_3\) aqueous solution. Additionally, the XRD pattern also showed the modified Pb electrode containing some derivatives after the electrodeposition which enhanced the stability of the TCE sensor. The optimal conditions for preparation working electrode were obtained as 0.1 M HNO\(_3\) pretreatment, 20 mA/cm\(^2\) electrodeposition current density, and 30°C electrodeposition temperature. Under the optimal sensing conditions, a linear response, \(i = 1.060C_{[\text{TCE}]} + 9.167\), was obtained under TCE concentration range from 100 to 700 ppm. Additionally, \(k\) is 7.217 × 10\(^{-4}\) cm\(^2\) s\(^{-1}\). Therefore, the electrochemical TCE sensor by using modified Pb electrode showed promising features for commercial application.