

SELECTIVE ANALYSIS OF COPPER AND SILVER IONS USING ELECTRODES MODIFIED WITH ZINC(II)-BENZENETRICARBOXYLATE NETWORKS

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ABSTRACT

For the sake of suppression of metallic surface chemistry and enhancement of selectivity of electrodes to certain species, noble metal electrodes were modified with the porous inorganic network: $Zn_3(BTC)_2 \cdot 12H_2O$, where BTC = benzenetricarboxylate. The network was applied to platinum electrodes as a PVC mixture or was prepared by heating or refluxing the reactants in the presence of platinum electrode. The modified electrodes confirmed the typical behavior expected from a modified electrode, where the distinct voltammetric features, which are characteristic for platinum electrodes, were suppressed. The modified electrodes showed remarkable selectivity towards both copper and silver ions. Detection limit for the analysis of copper ions on the modified electrodes was found to be 1.10×10^{-5} M. Those electrodes showed extraordinary recognition to concentrations of silver ions as low as 5.10×10^{-10} M.

Keywords: modified electrodes, porous networks, Zn(II)-benzenetricarboxylate, copper ion analysis, silver ion analysis, selective recognition.

1. INTRODUCTION

A vast number of publications in the last three decades was dedicated to modification of solid surfaces on premise that the modification may enhance catalytic properties, induce surface passivation for corrosion inhibition or modify selectivity and reactivity of the solid surfaces for electrocatalytic and electroanalytical applications.⁽¹⁻¹³⁾

Yaghi and co-workers prepared porous inorganic frameworks with microstructures

containing pores, channels, or layer spacing of molecular dimensions.⁽¹⁴⁻¹⁹⁾ These molecular gateways, which show high resemblance to zeolites, may impart a selective screening of some guest compounds or ions. Screening of ions or molecular recognition in the host network might be on the basis of size, shape or charge of the guest.^(2, 9-12)

The present work aims at preparation, characterization of platinum electrodes modified with a zinc-organic network $Zn_3(BTC)_2 \cdot 12H_2O$ where BTC stands for benzene tricarboxylate group.⁽¹⁶⁾ The microporous trimesic acid-zinc(II) network $Zn_3(BTC)_2 \cdot 12H_2O$ was first synthesized by Yaghi and co-workers in 1996.⁽¹⁶⁾ Its structure is composed of zigzag chains constructed from two symmetry-inequivalent $M(H_2O)_4^{2+}$ units and BTC ligands.

2. EXPERIMENTAL

2.1 Instrumentation:

A 362-potentiostat (Princeton Applied Research), interfaced with CondeconTM 310 interface (EG & G Instruments Ltd.) to a computer, was used for electronic control and data acquisition. Voltammetric experiments were conducted using a conventional, H-shaped, three-electrode cell equipped with a multiple-inlet system for admission of supporting electrolyte and for purging and blanketing the solution with oxygen-free nitrogen, in addition to the admission of solutions in the cell without exposing the working electrode to ambient atmosphere.

The reference electrode was Ag/AgCl/1.0 M Cl^- and all the reported potentials are referenced to this electrode. The working electrode used was polycrystalline platinum (0.5 mm-diameter, 99.99% pure, Johnson Matthey) rounded at the end or shrouded in PTFE to provide a reproducible surface area upon immersion beneath the surface of the solution in the working electrode compartment. The auxiliary electrode was a glass-fitted platinum spiral wire (99.99% pure, Johnson Matthey).

The purged supporting electrolyte and all the solutions used were dispensed into the electrochemical cell from shelved bubblers by gravity action. All tubes used for nitrogen purging or for conveying solutions to the cell were made of PTFE (Cole

Parmer).

DPV experiments were carried out using a 746 VA Trace Analyzer (Metrohm, Switzerland), modified by replacing the mercury electrode with the modified electrode.

2.2 Materials:

All reagents used were analytical grade chemicals supplied by various companies and were used without further purification. Test cations and compounds were standard solutions of high-purity chemicals supplied by BDH and were used as received.

The gases used were of ultrapure quality supplied by The Industrial and Medical Liquid Gas. The gas cylinders were coupled with Oxosorb cartridges (Supelco) for removal of traces of oxygen.

All solutions were made from the reagents dissolved in triply distilled water where the second distillation was carried out from basic potassium permanganate solution to destroy any organic impurities.

2.3 Procedures:

2.3.1 Surface pretreatment and modification

The electrode surface was initially cleaned in a freshly prepared chromic acid solution, rinsed with triply distilled water, and placed in the H-shaped conventional electrochemical cell that contained a purged solution of 0.5 M H₂SO₄. The electrode surface was conditioned by cyclization the electrode potential between -0.20 and +1.30 V to remove surface impurities. Surface cleanliness was verified by reproduction of the voltammogram of platinum polycrystalline surface electrode at slow scan rate.⁽²⁰⁾

As a reference point for characterization of the modified electrode, the solid Zn₃(BTC)₂·12H₂O network was prepared according to the procedure described by Yaghi et al.⁽¹⁶⁾ The identity of the network was verified by reproducing the IR spectrum (Figure 1) where an excellent agreement between the produced spectrum and the published spectrum. Zn₃(BTC)₂·12H₂O network was mixed with PVC in a 1:1 ratio, dissolved in acetone, and a drop of the slurry was applied to the voltammetrically verified-clean electrode. On drying in a nitrogen-filled dessicator at ambient conditions the electrode

was transferred to the cell for further experimentation. This technique for preparation of the electrode is one of the simplest approaches to modification of the modified electrode where the applied layer lacks mechanical durability and lacks readiness to control of the thickness of the modifier-PVC layer. This electrode, however, provided a reference behavior to compare with our succeeding prepared electrode. The adsorptive behavior of the starting materials at platinum electrode was investigated too to find the grounds for discrimination between adsorbed starting materials and formed network.

The electrode was modified with a microporous zinc trimesic acid network, $Zn_3(BTC)_2 \cdot 12H_2O$ following the same procedure reported by Yaghi and co-workers with the exception of placing a platinum wire. An aqueous mixture (15.0 mL) of hydrated Zn(H) acetate (0.360 g, 1.65 mmol) and H_3BTC (0.200 g, 0.950 mmol) was placed in a sealed stainless steel vessel, which was heated in a furnace according to a specific temperature regime.⁽¹⁶⁾ The electrode was taken out from the reaction vessel, washed with water and inserted into the electrochemical cell for further experimentation. Another approach which gave very similar results involved refluxing the reactants for about 10 hours in presence of a platinum wire.

3. RESULTS:

3.1 Features of the modified electrode

Figure 2 shows the cyclic voltammogram of polycrystalline platinum modified with $Zn_3(BTC)_2 \cdot 12H_2O$ network. The voltammogram has different voltammetric features from those of the starting materials at platinum electrode. Upon leaving the electrode immersed in the solution in the cell for an hour or longer, an anodic peak centered at 0.08 V and its cathodic counter peak centered at -0.06 V were observed. These peaks grew gradually upon leaving the electrode under purging in the cell and decreased gradually on cyclization of the electrode potential (Figure 3) between -0.2 and 0.2 V. These peaks were analyzed in terms of the separation between the anodic and cathodic peaks, ΔE . ΔE was plotted against the scan rate (v) and the line was extrapolated to give ~ 60 m V at $v=0$ indicating a 1-electron process. XPS using sigma

microprobe investigations indicated the presence of silver in the coat (Figure 4). The presence of silver in the network is attributed to a leak of a very minute amount of silver ions from the reference electrode when the reference electrode was housed in a single compartment cell containing the three electrodes. The appearance of silver peaks was largely enhanced by presence of silver ions in the solution (Figure 5). Further evidence for ascribing these peaks to silver ions was obtained by trapping AgNO_3 in a PVC matrix using acetone as a solvent (Figure 6). The voltammogram of this electrode shows two peaks similar to those observed for the network (Figure 3). The electrode seemed very prone to sequester silver from the solution and the gradual growth of the peaks demonstrated the porous nature of the coat. The peak current showed also mutual dependence on $v^{1/2}$ and v indicating a diffusion-controlled surface process. The emergence of silver peaks for the modified electrodes prepared by heating the reactants in presence of the electrode and for electrodes prepared by trapping the network in PVC matrix atop of the electrode indicated that the formed film at the surface is $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ network.

Further experimentation on modified electrodes was conducted using a 400 μm monochromated Al Ka X-ray source XPS analyser. Two samples of the modified electrodes were prepared, one which showed the silver peaks (A) and the other showed no silver peaks (B). The XPS spectra of the two samples are shown in Figures 4 and 7, respectively. Depth profiling was carried out by sputtering argon ions with a current of 4 μA , with a sputter period of 60 s between each etch level. The gas flow (8×10^{-8} mbar) was set by opening an argon leak valve manually. The XPS depth profiles for both samples are shown in Figures 8 and 9, respectively.

The percent atomic concentrations of the elements at the top of the modified platinum electrodes are plotted against sputtering time, representing levels (Figures 10 and 11). Depth profiling of silver in the sample whose voltammogram shows silver peaks is shown in Figure 12.

There are significant differences between the two samples. Zinc is present in

sample whose voltammogram didn't show silver peaks. In fact, there is still a trace of zinc presence after over 160 levels, indicating a relatively thick network layer. The other sample, whose voltammogram shows silver peaks, initially shows no zinc, but a strong initial presence of silver.

One of the two platinum samples was scratched at the top with a clean scalpel and the XPS spectrum was carried out for the resultant freshly damaged area. As expected, a nearly clean platinum surface was acquired from this area (Figure 13).

Figure 14 shows electron micrographs for some $Zn_3(BTC)_2 \cdot 12H_2O$ network-modified platinum electrodes. Some of these micrographs show deep grooves indicating that a thick coating which agrees with the depth profiling XPS data.

3.2 Electrode Response to some test organic and inorganic molecules:

Cyclic voltammetry at the modified electrodes was used to test the electrode's response to some common organic compounds. The tested organic molecules were acetone, acetonitrile, benzene, carbon tetrachloride, methanol, ethanol, hydrazine, tetrahydrofuran, formaldehyde, and formic acid. The voltammograms of the modified electrodes showed no change upon exposure to a supporting electrolyte solution containing the above-mentioned compounds at 1.0×10^{-3} M concentration.

Other experiments included the study of the adsorption behavior of methanol and hydrazine. The adsorption of methanol (1 %) was examined at open circuit and potentiostatically at -0.3 – 0.6 V for 10 min. The produced voltammograms were not different from that of the plain modified electrode.

Adsorption behavior of some small gaseous molecules such as carbon monoxide and oxygen were also investigated. The electrode was dosed with CO from a CO-saturated 0.5 M KCl solution at open circuit or potentiostatically at -0.3 – 0.6 V for 10 min. The cyclic voltammogram, recorded in CO-saturated 0.5 M KCl, showed an anodic hump centered at about 0.3 V, with its cathodic counter peak centered at 0.2 V (Figure 15). Purging the 0.5 M KCl solution with oxygen for 100-160 min. at open circuit did not affect the potentiodynamic E-i trace. Presence of surfactants also such as dodecyl

sulfate, $C_{12}H_{25}O_4S^-$, (sodium salt, with concentrations of 3.78×10^{-2} up to 7.55×10^{-2} M) and sodium salt of pentanesulfonic acid, $C_5H_{11}O_3S^-$, ($6.62 \times 10^{-2} - 1.32 \times 10^{-1}$ M) did not change the voltammetric features of modified electrodes in 0.5 M KCl solution.

3.3 Response to cations:

Cyclic voltammetry and differential pulse voltammetry were applied to test the response of electrodes modified with $Zn_3(BTC)_2 \cdot 12H_2O$ network towards metal ions. The modified platinum electrode was irresponsive to chromium (III), cadmium(II), lead(II), zinc(II), nickel(II), cobalt(III), manganese(II) and gold (I).

3.3.1 Silver ion

As it was mentioned above, the modified platinum electrode was very sensitive to the presence of silver. Though the expected concentration of silver(I) in a 0.50 M KCl as calculated from the solubility product constant is $\sim 2 \times 10^{-12}$ M, this very low concentration (0.2 pmol per trillion) was enough to be detected by differential pulse voltammetry. Figure 16 shows the differential pulse voltammetric response to a solution containing 5.1×10^{-10} M Ag^+ . For higher concentrations, a linear relationship between the silver peak current and concentration is disclosed (Figure 17 A and B).

3.3.2 Copper ion:

Cyclic voltammetry at the modified platinum electrode was applied for analysis of copper ion. Differential pulse voltammetry and anodic stripping analysis were applied to analyze copper too. The cyclic voltammograms of modified platinum electrode in presence of 2.63×10^{-4} and 3.15×10^{-4} M Cu^{2+} are shown in Figure 18, while the differential pulse voltammograms are shown in Figure 19 where excellent linearity between peak current and concentration is disclosed.

Real water sample from Zarqa River whose copper concentration is below the detection limit by AAS was spiked with a standard Cu^{2+} solution to provide a solution whose copper concentration is 7.87×10^{-5} M. This sample was analyzed at the modified electrode and the determined copper concentration was 8.46×10^{-5} M. Atomic absorption spectroscopic analysis of Cu^{2+} in this sample amounted to a value of $8.09 \times$

10^{-5} M. The percentage difference between the two methods was about 4.6 %, which attests to the accuracy of the analysis at the modified electrode.

The presence of many tested organic compounds, such as acetone, acetonitrile, benzene, carbon tetrachloride, methanol, ethanol, tetrahydrofuran, formaldehyde, formic acid, sodium salts of dodecyl sulfate and pentanesulfonic acid, carbon monoxide and oxygen did not affect the analysis of copper.

Presence of Pb^{2+} , Cd^{2+} , Ni^{2+} , Co^{3+} , and Cr^{3+} ions enhanced the copper peak current, which was surmounted by using the standard addition technique. Other cations such as silver, iron, zinc, manganese, calcium, and gold ions did not affect the position or magnitude of the copper peak.

3.3.3 Ferric ion:

Anodic stripping differential pulse voltammetry was used for analysis of Fe^{3+} at the modified platinum electrode (Figure 20). The preconcentration step was conducted at -0.3 V for five minutes. The calibration curve was established with excellent linearity ($R = 0.9955$) for an optimal concentration range of $(1.79 - 10.71) \times 10^{-4}$ M.

Table 1 summarizes the regression coefficients and detection limits for the analysis of copper, silver, and iron ions on modified electrodes.

4. CONCLUSIONS

The findings of the present work can be summarized as follows

- Thin coating of $Zn_3(BTC)_2 \cdot 12H_2O$ network at platinum surfaces were prepared to the first time.
- The modified surfaces were characterized by XPS and voltammetry. The porous nature of these electrodes was disclosed by XPS and cyclic voltammetry.
- Exploration of analytical applications of these electrodes in electroanalysis showed that these electrodes might be used as voltammetric sensors for analysis of silver and copper and iron.

ACKNOWLEDGEMENTS

The help of VG Scientific by performing the XPS analysis is highly appreciated.

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Table 1: Analytical parameters for the analysis of copper, silver, and iron ions on the modified platinum electrode.

Metal Ion	Electrochemical Technique	Regression Coefficient (R^2)	Detection Limit	
			mol.L ⁻¹	ppm
Fe ³⁺	ASV, DPV	0.9955	1.51×10^{-4}	8.85
Ag ⁺	CV	0.9847	9.27×10^{-5}	10.00
Ag ⁺	ASV, DPV	0.9755	5.10×10^{-10}	5.50×10^{-5}
Cu ²⁺	CV	0.9968	4.06×10^{-5}	2.58
Cu ²⁺	CV*	0.9939	4.17×10^{-5}	2.65
Cu ²⁺	ASV, CV	0.9928	2.36×10^{-5}	1.50
Cu ²⁺	DPV	0.9928	1.10×10^{-5}	0.70
Cu ²⁺	CV**	0.9969	9.10×10^{-5}	5.78
Cu ²⁺	CV***	0.9951	4.28×10^{-5}	2.72

* The silver peaks were observed on the voltammograms prior to analysis.

** Prepared using the network / PVC method.

*** Prepared using the 10-min reflux method.

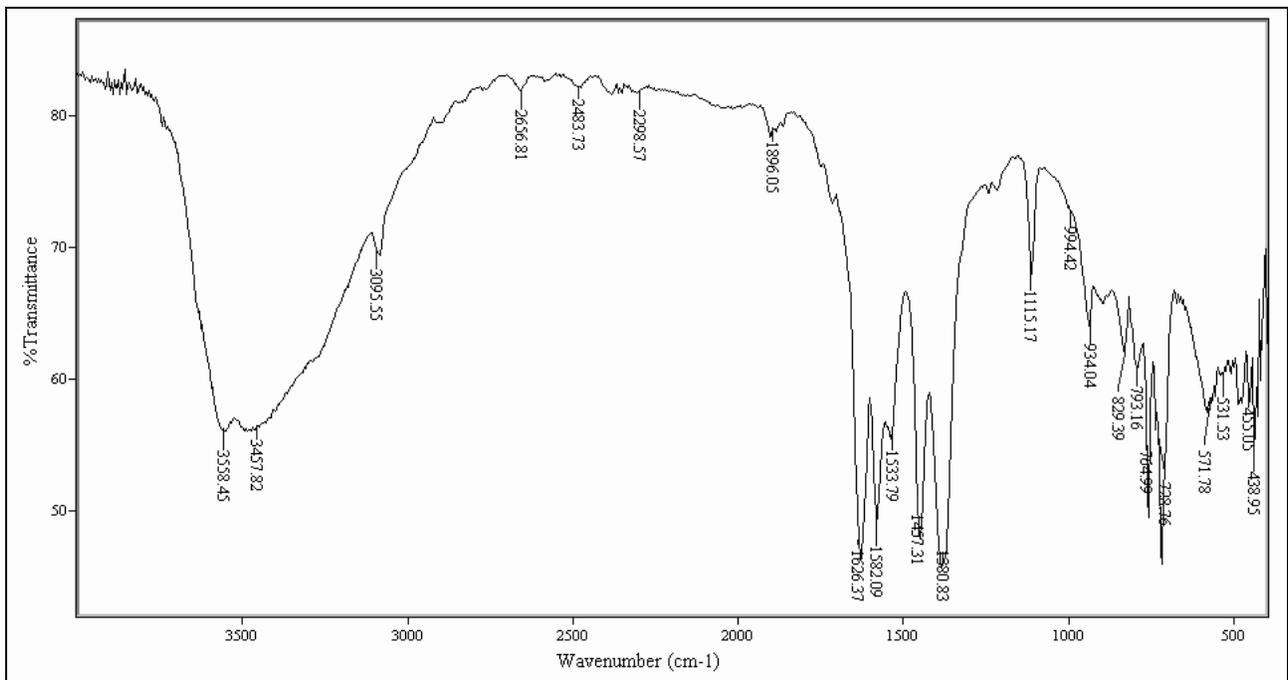


Figure 1: The Infrared spectrum of Zn₃(BTC)₂·12H₂O network (in KBr).

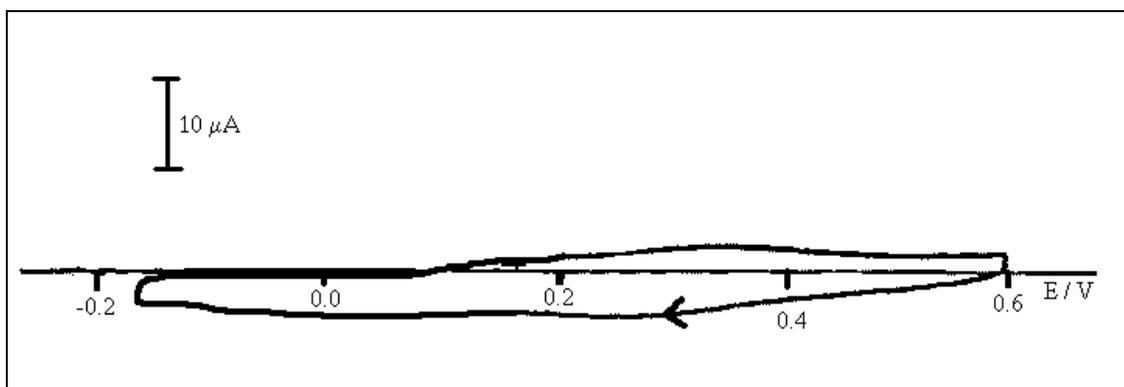


Figure 2-A: Cyclic voltammogram of platinum electrode modified with $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ in 0.5 M KCl . Scan rate = 50 mV/s .

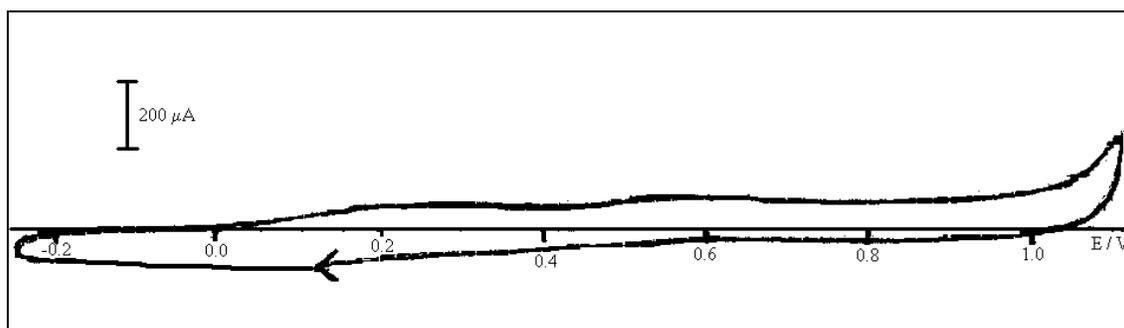


Figure 2-B: Cyclic voltammogram of platinum foil electrode modified with $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ in 0.5 M KCl using 10-hour reflux method. Scan rate = 50 mV/s .

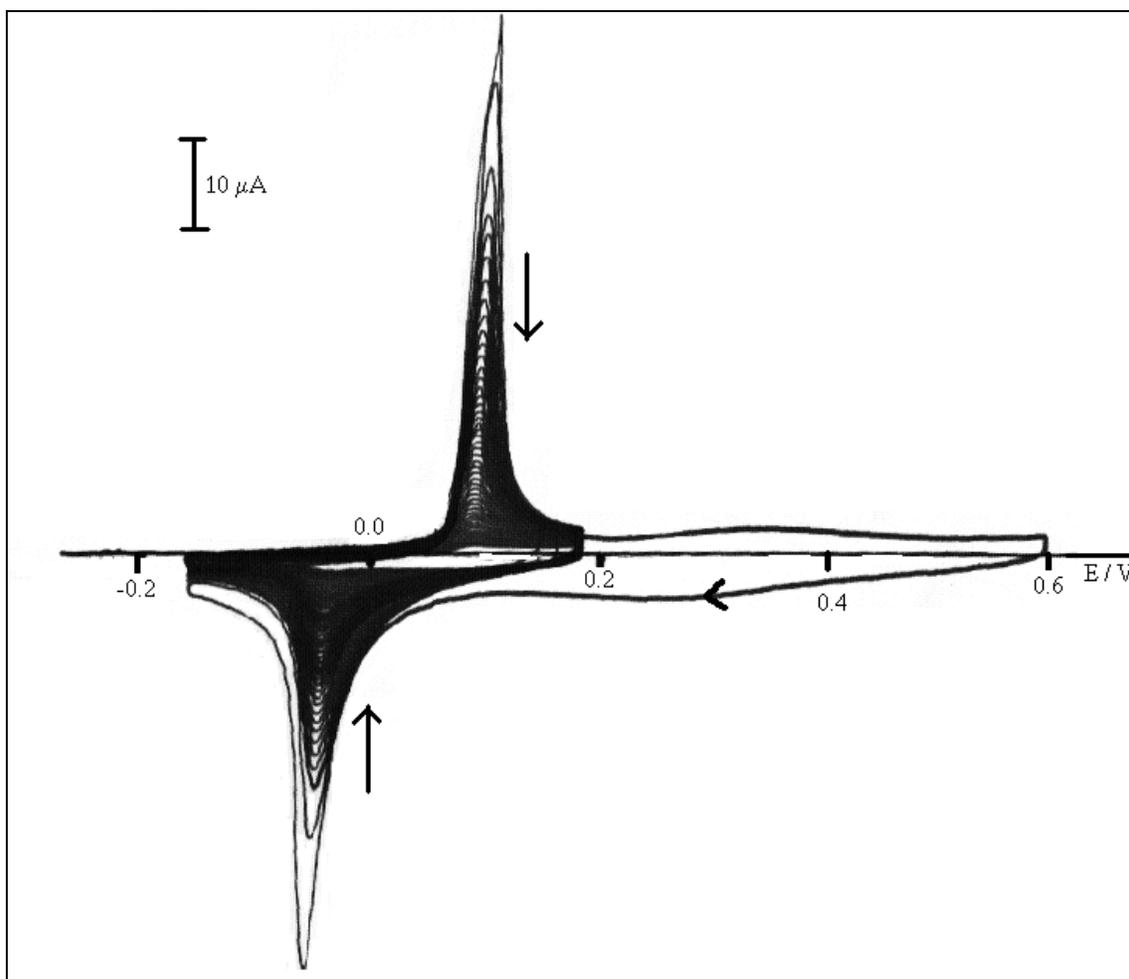


Figure 3: Cyclic voltammogram of platinum electrode modified with $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ in 0.5 M KCl. The voltammogram shows many cycles at scan rate of 50 mV/s.

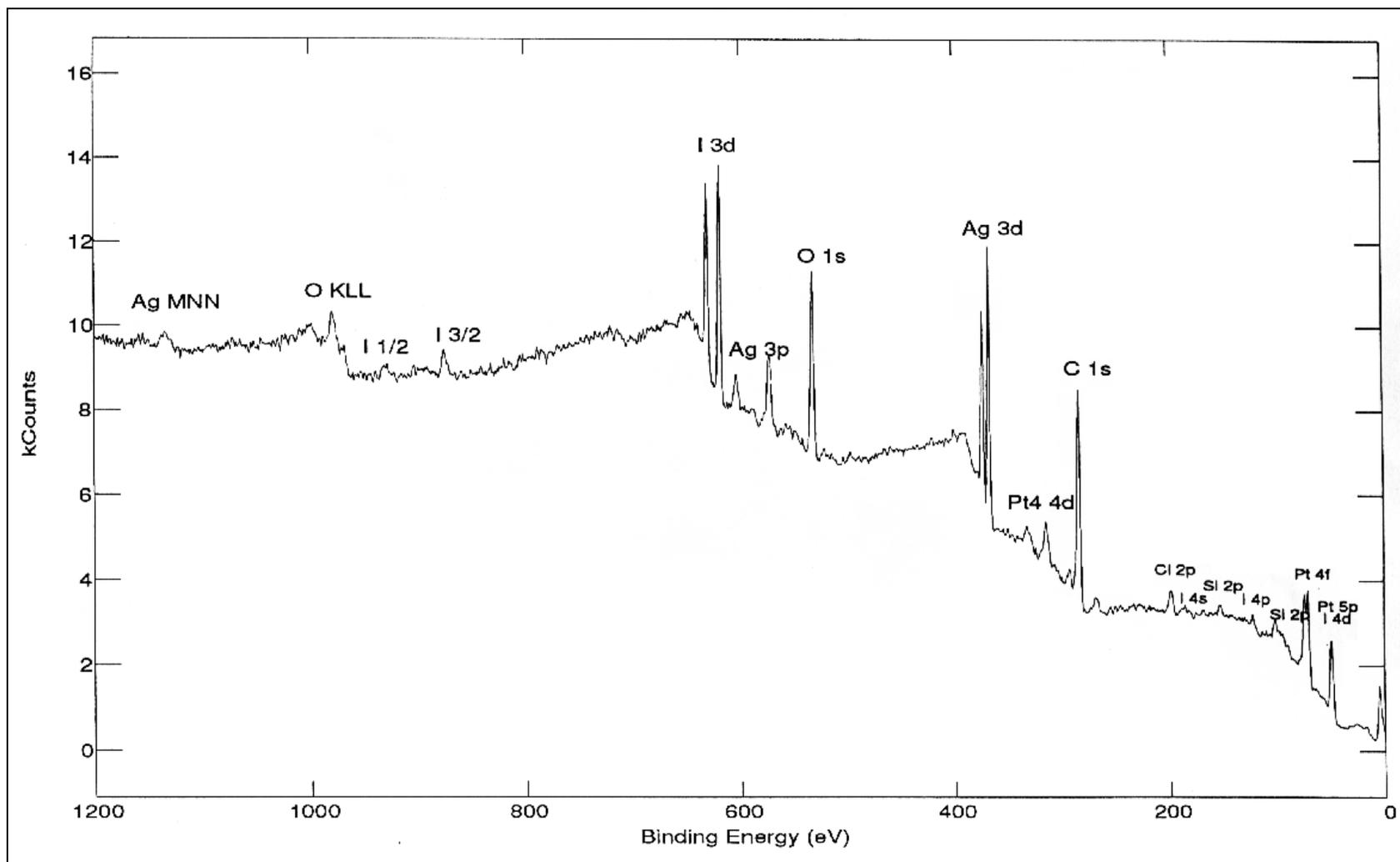


Figure 4: XPS spectrum of the top of modified platinum wire (A) whose cyclic voltammogram shows silver peaks.

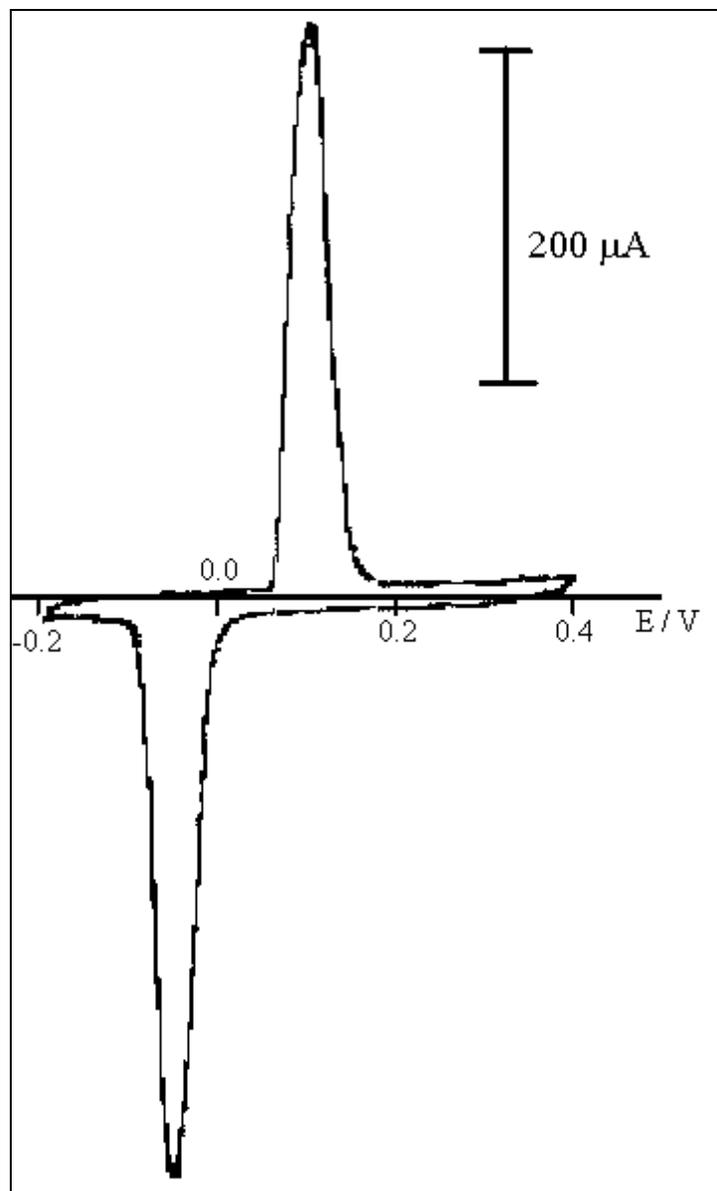


Figure 5: Cyclic voltammogram of platinum electrode modified with $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ in $0.5 \text{ M KCl} + 9.27 \times 10^{-5} \text{ M Ag}^+$ solution. The voltammogram was recorded in Ag^+ -free 0.5 M KCl . Scan rate = 50 mV/s .

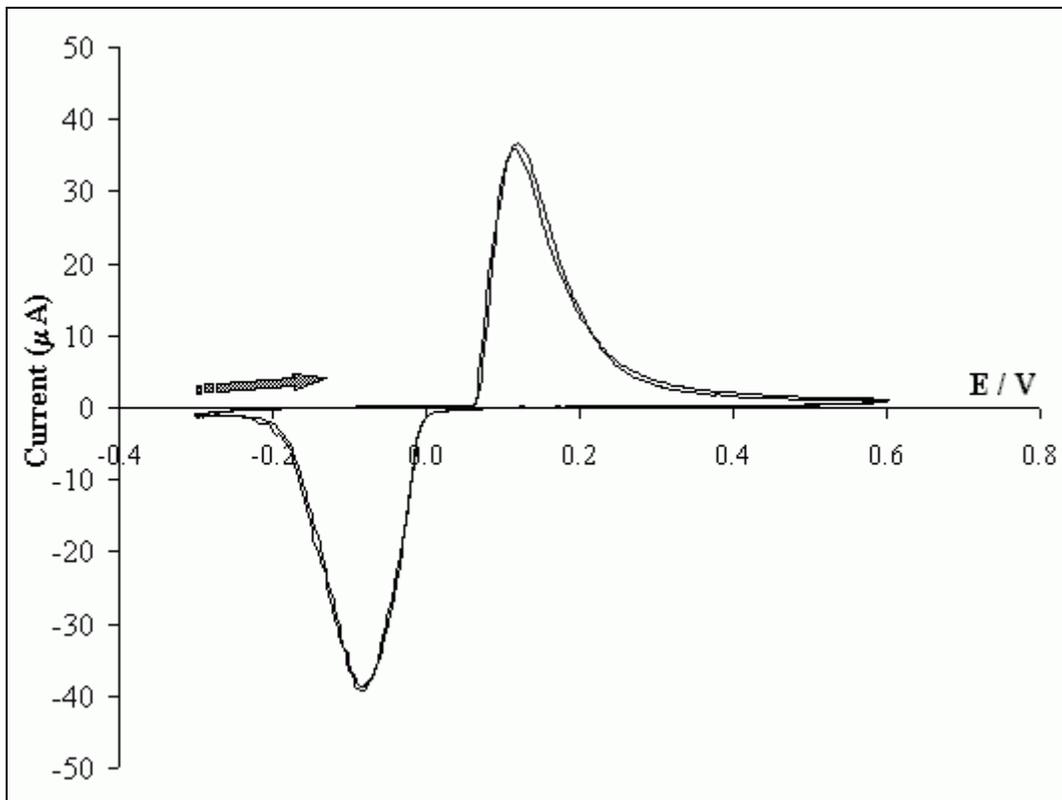


Figure 6: Cyclic voltammogram of platinum electrode modified with AgNO_3 / PVC mixture in 0.5 M KCl. Scan rate = 50 mV/s.

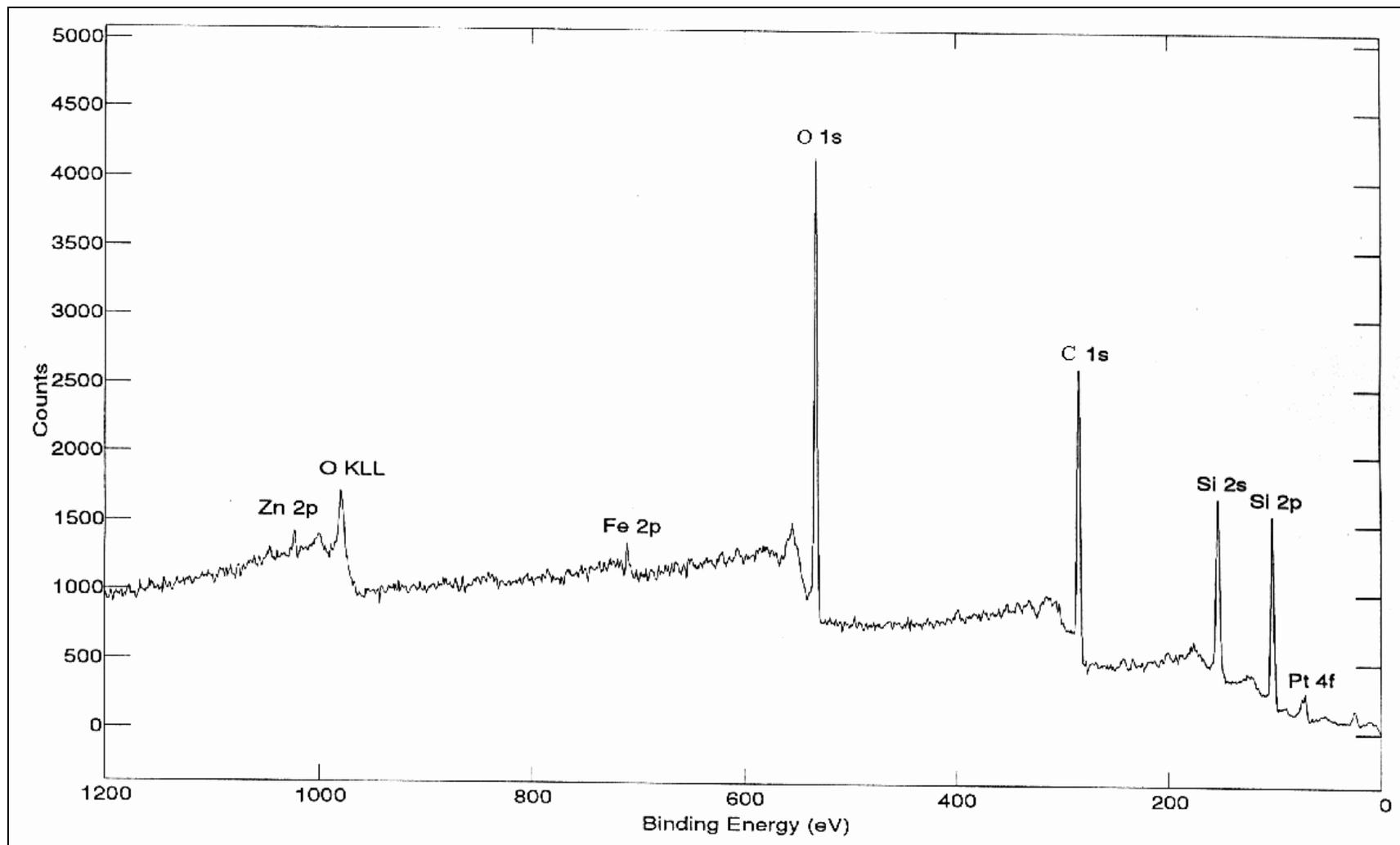


Figure 7: XPS spectrum of the top of modified platinum wire (B) whose cyclic voltammogram shows no silver peaks.

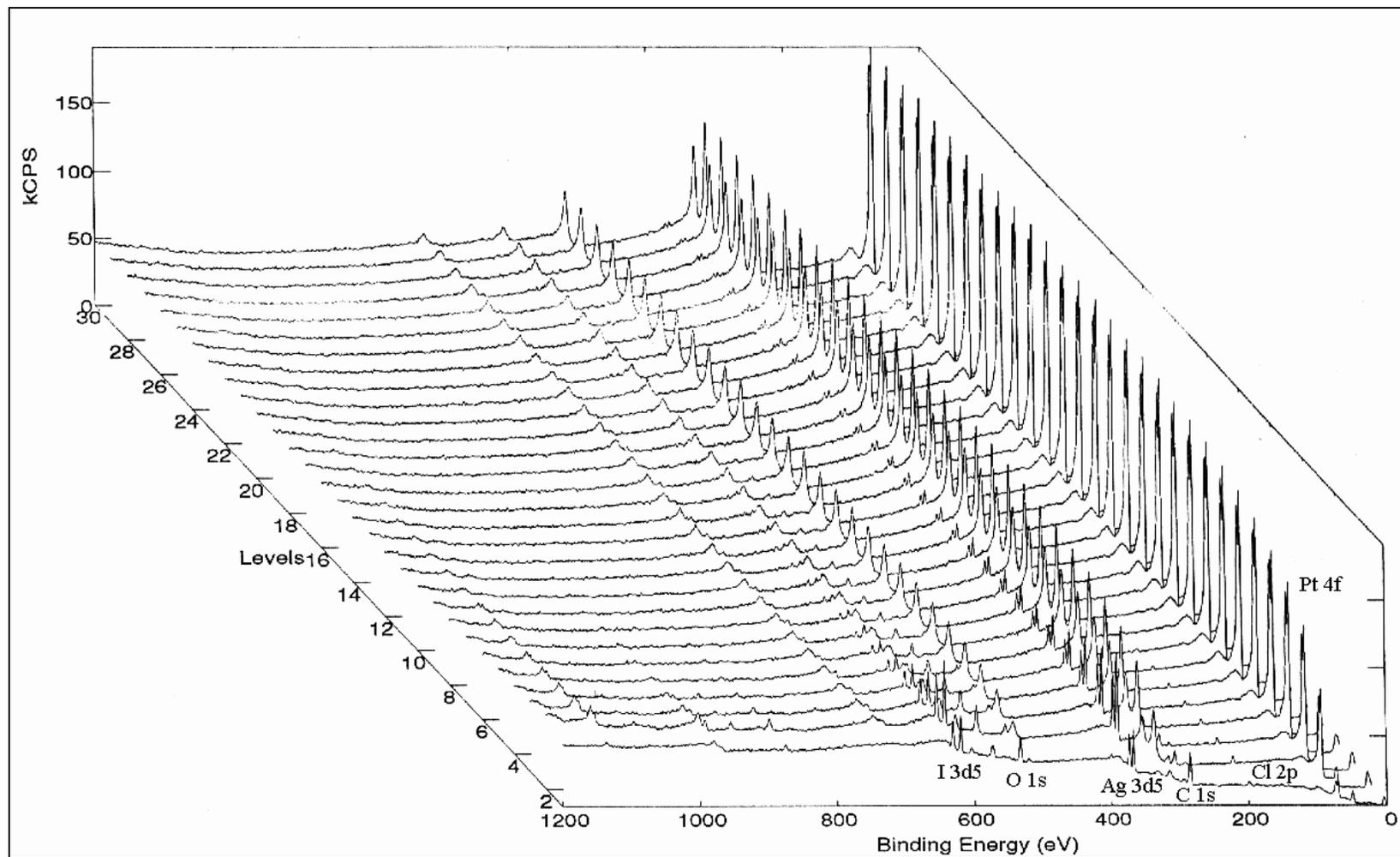


Figure 8: XPS depth profile spectrum, showing levels 1–30, of the top of modified platinum wire (A).

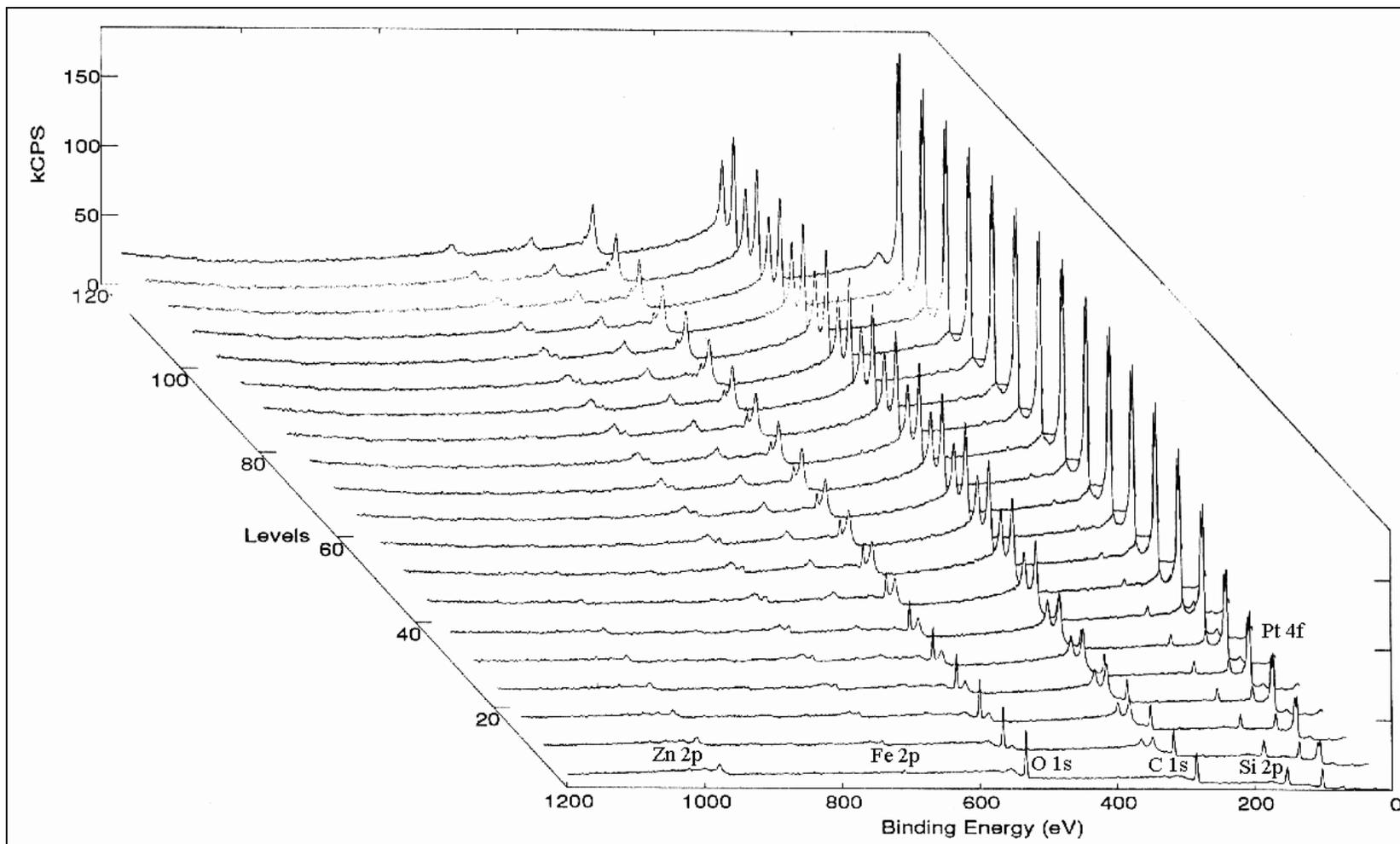


Figure 9: XPS depth profile spectrum, showing levels 1–120, of the top of modified platinum wire (B).

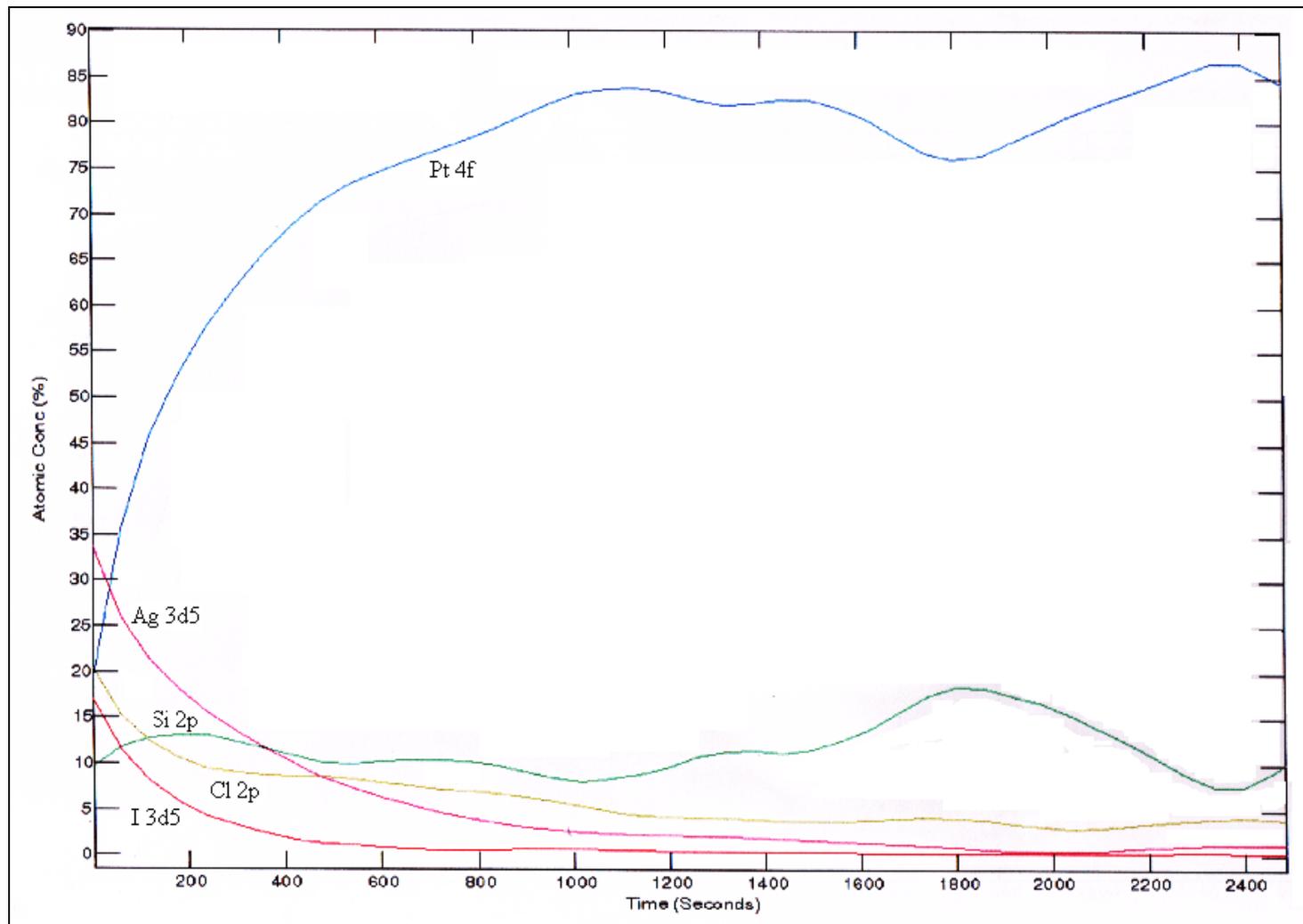


Figure 10: Variation in atomic concentration with etch-time for the sample (A).

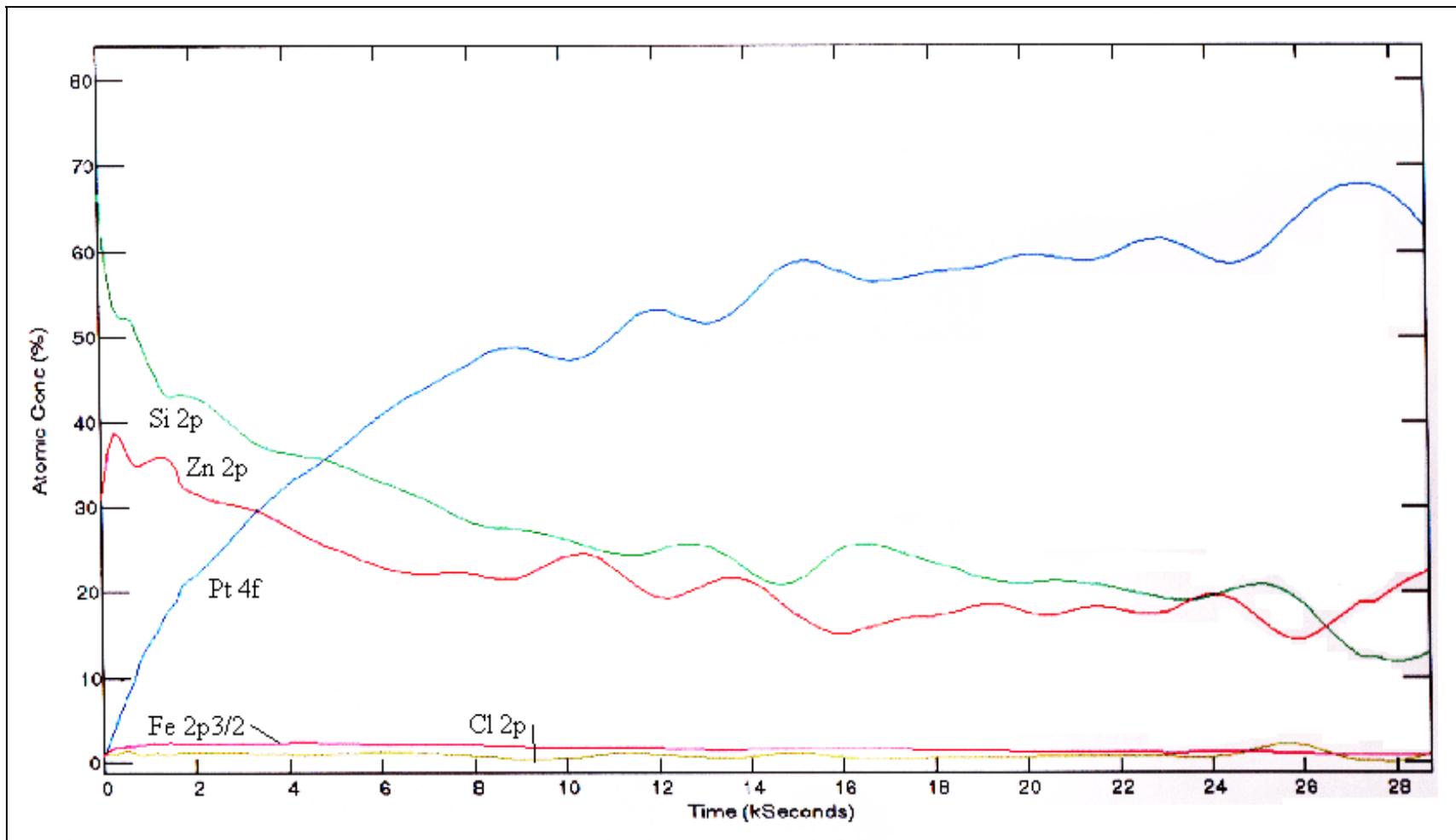


Figure 11: Variation in atomic concentration with etch-time for the sample (B).

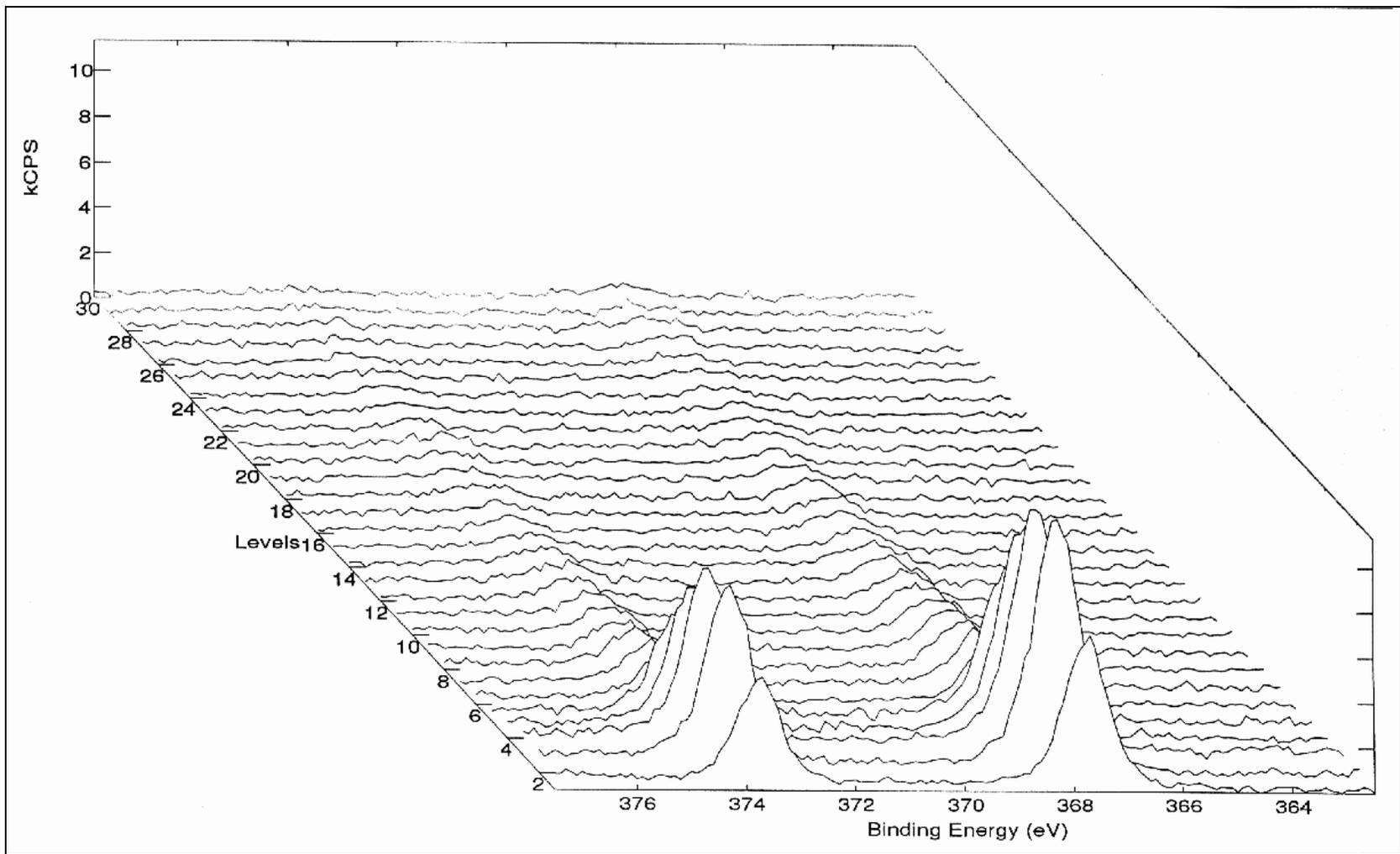


Figure 12: Silver 3d⁵ peak XPS depth profile spectrum, enlarged from Figure 8.

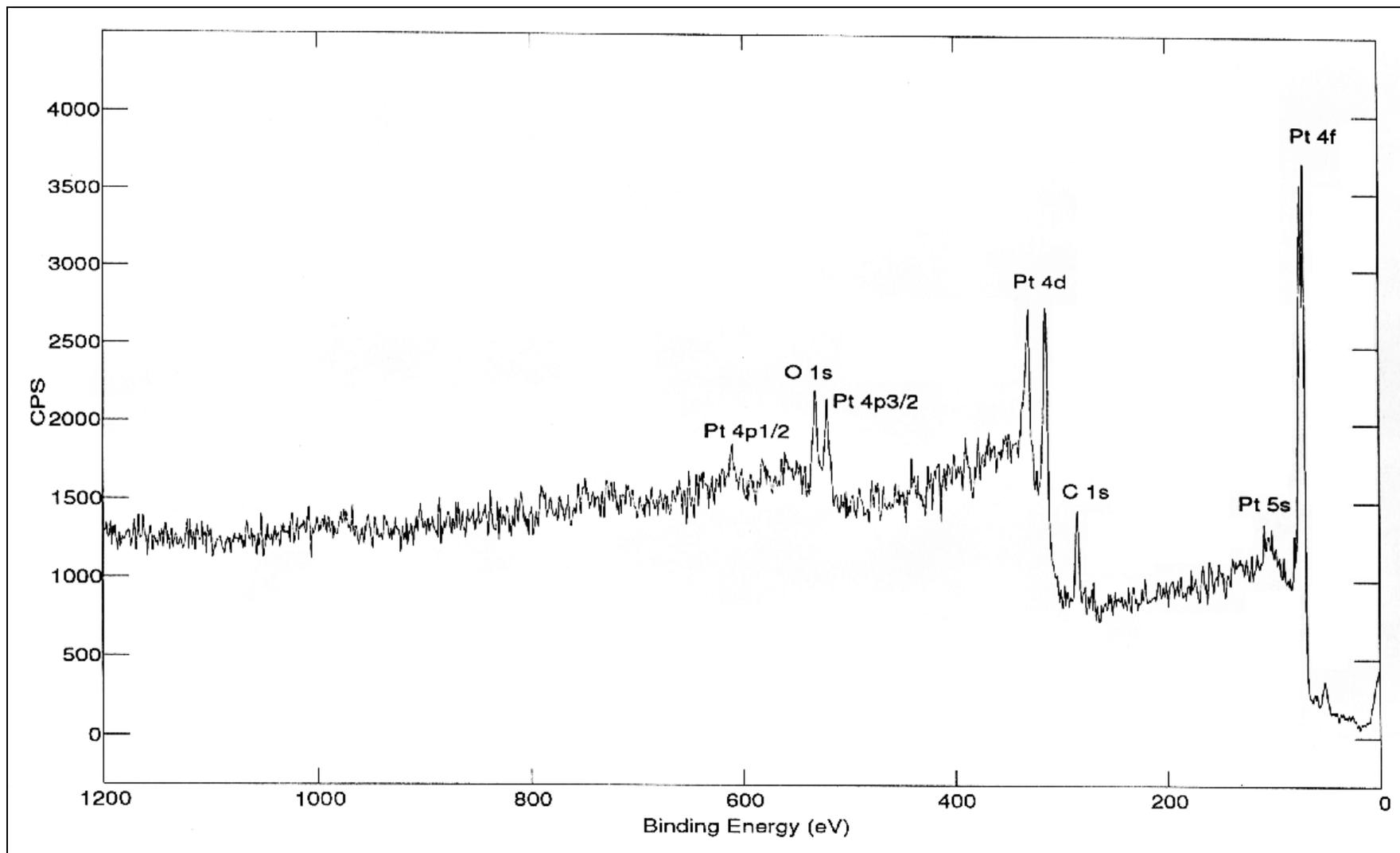


Figure 13: XPS spectrum of the top of modified platinum wire, after scratching the top of the wire with a scalpel.



Figure 14: Scanning Electron Microscope micrographs of samples of the modified platinum surfaces.

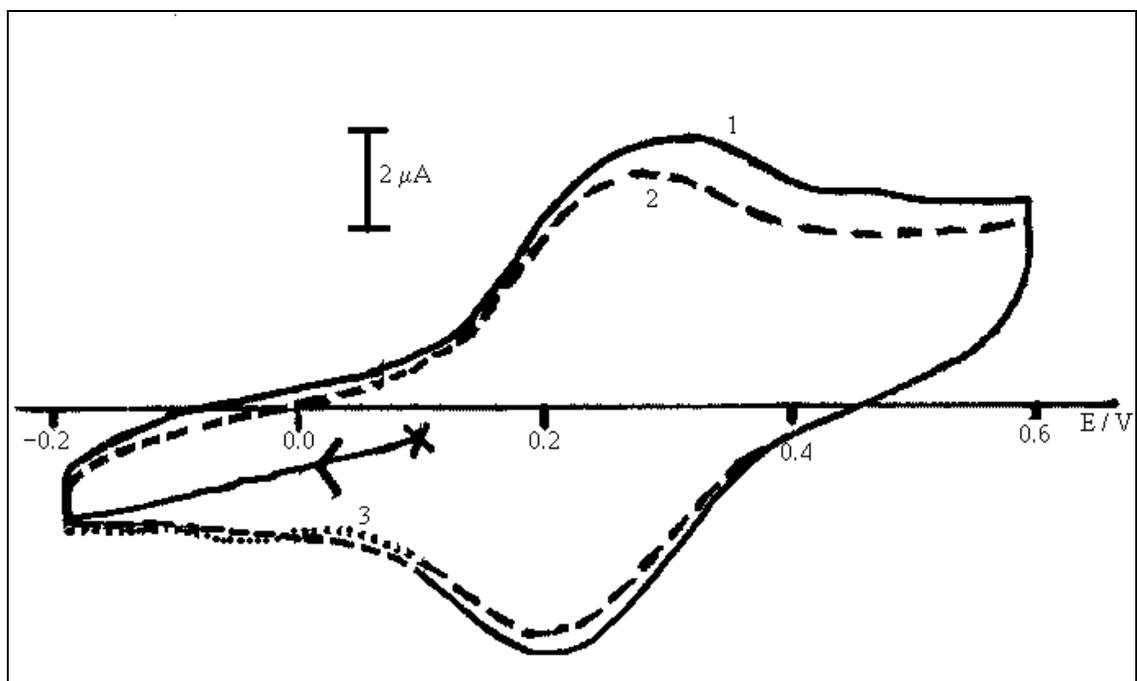


Figure 15: Cyclic voltammogram of platinum electrode modified with $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ in 0.5 M KCl saturated with carbon monoxide for 10 min. at 0.1 V. The cyclic voltammogram was recorded in CO-saturated 0.5 M KCl. Scan rate = 50 mV/s. —: 1st scan; -----: 2nd scan;: 3rd scan.

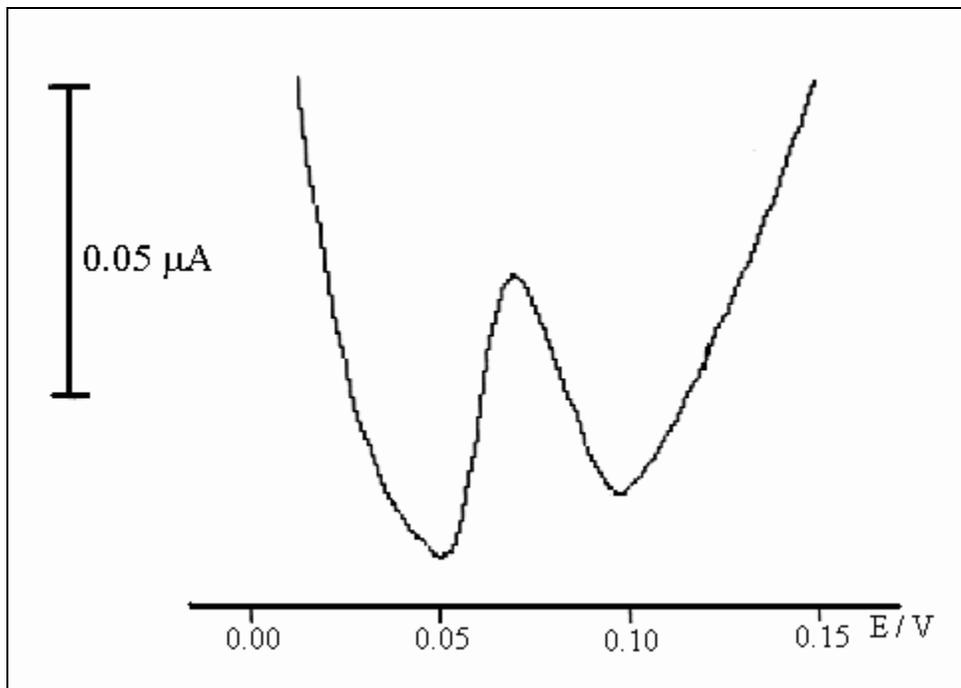


Figure 16: Differential pulse voltammogram of platinum electrode modified with $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ in 0.5 M KCl + 5.10×10^{-10} M Ag^+ solution at -0.30 V for 30 min. Scan rate = 6.67 mV/s.

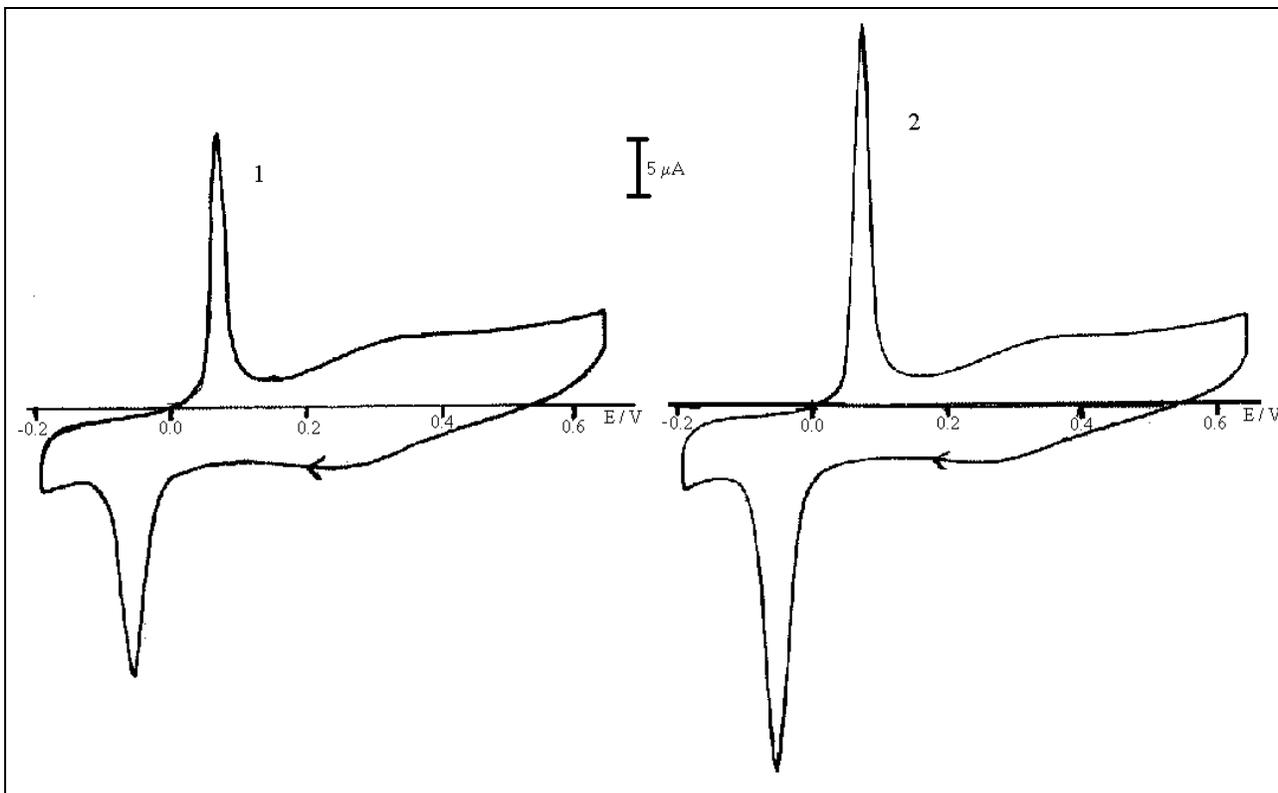


Figure 17-A: Cyclic voltammograms of platinum electrode modified with $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ in 0.5 M KCl + Ag^+ solutions at 50 mV/s. 1: $[\text{Ag}^+] = 1.52 \times 10^{-4}$ M, 2: $[\text{Ag}^+] = 1.82 \times 10^{-4}$ M.

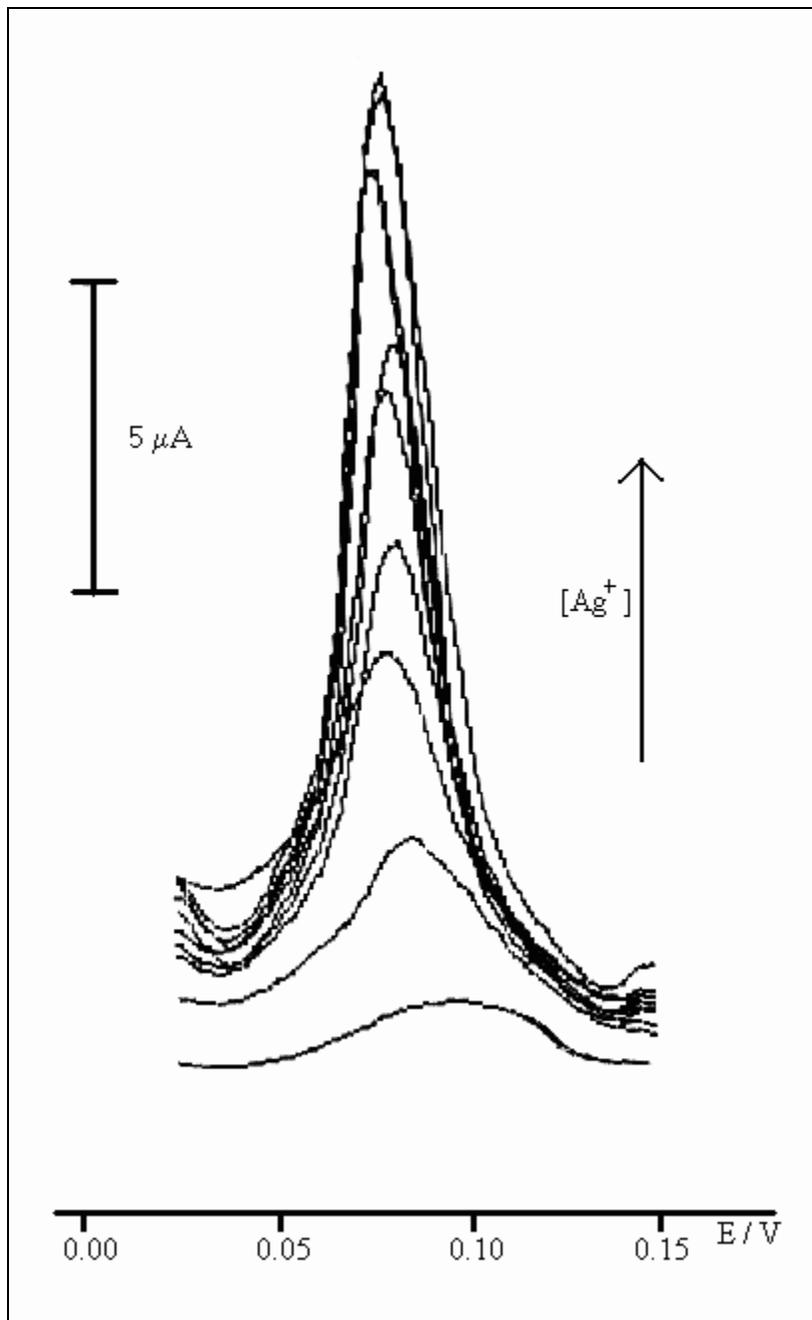


Figure 17-B: Differential pulse voltammograms of platinum electrode modified with Zn₃(BTC)₂·12H₂O in 0.5 M KCl + $(0.46 - 4.63) \times 10^{-6}$ M Ag⁺ solutions. The electrode potential was held at -0.30 V for 5 min. Scan rate = 6.67 mV/s.

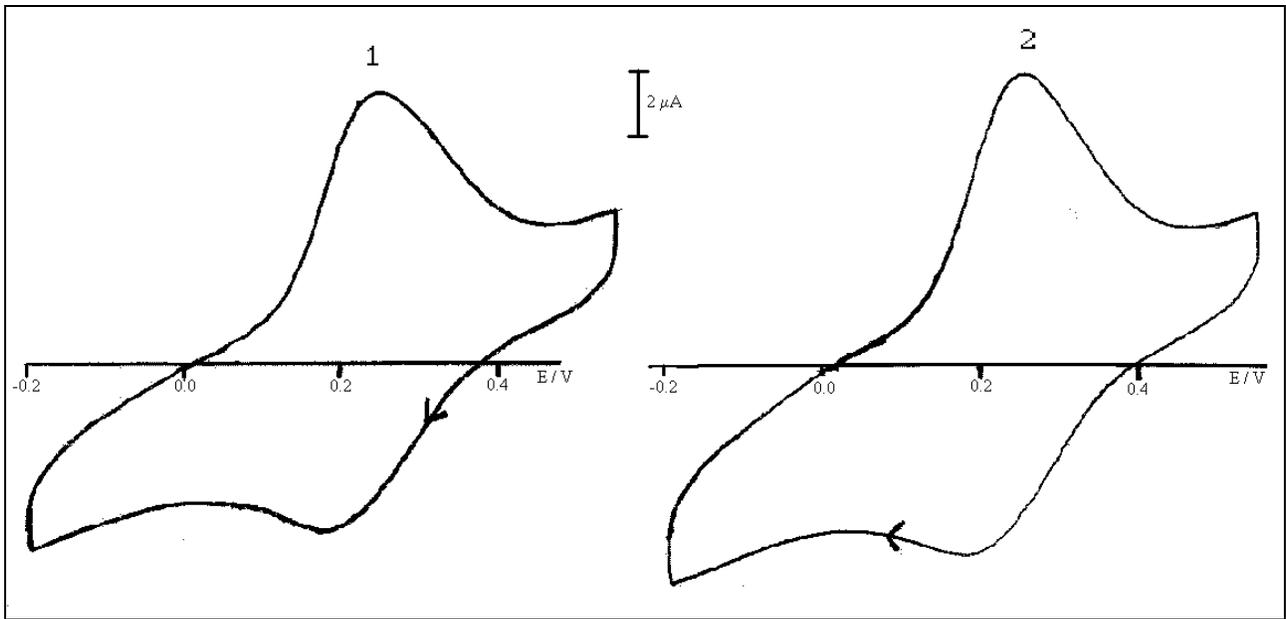


Figure 18: Cyclic voltammograms of platinum electrode modified with $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ in 0.5 M KCl + Cu^{2+} solutions at 50 mV/s. 1: $[\text{Cu}^{2+}] = 2.63 \times 10^{-4}$ M, 2: $[\text{Cu}^{2+}] = 3.15 \times 10^{-4}$ M.

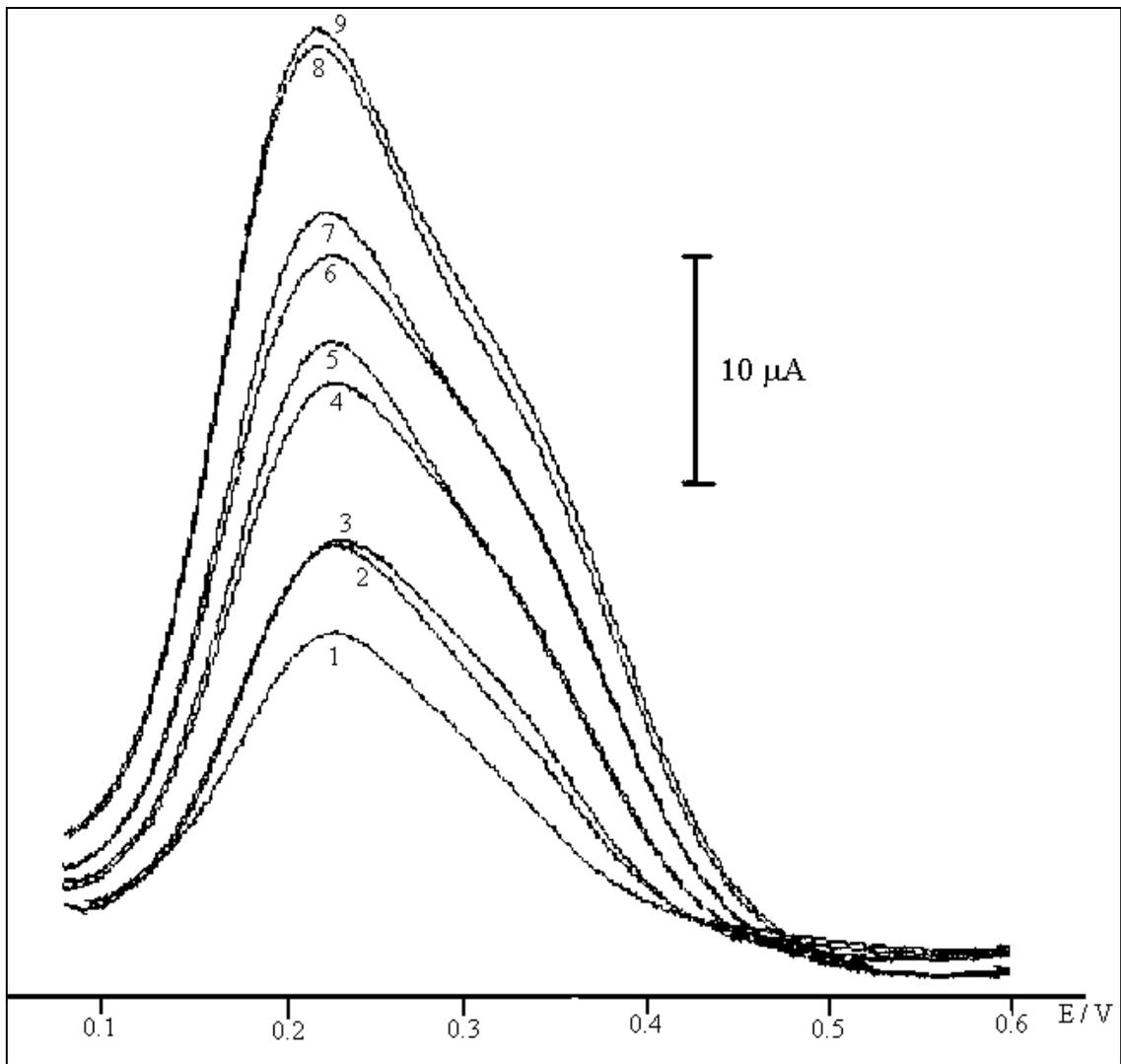


Figure 19: Differential pulse voltammograms of platinum electrode modified with $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ in 0.5 M KCl + Cu^{2+} solutions at 6.67 mV/s. The solution concentrations are ($\times 10^4$ M): 1: 0.79; 2: 1.18; 3: 1.57; 4: 2.36; 5: 3.15; 6: 3.94; 7: 4.72; 8: 6.30; 9: 7.87.

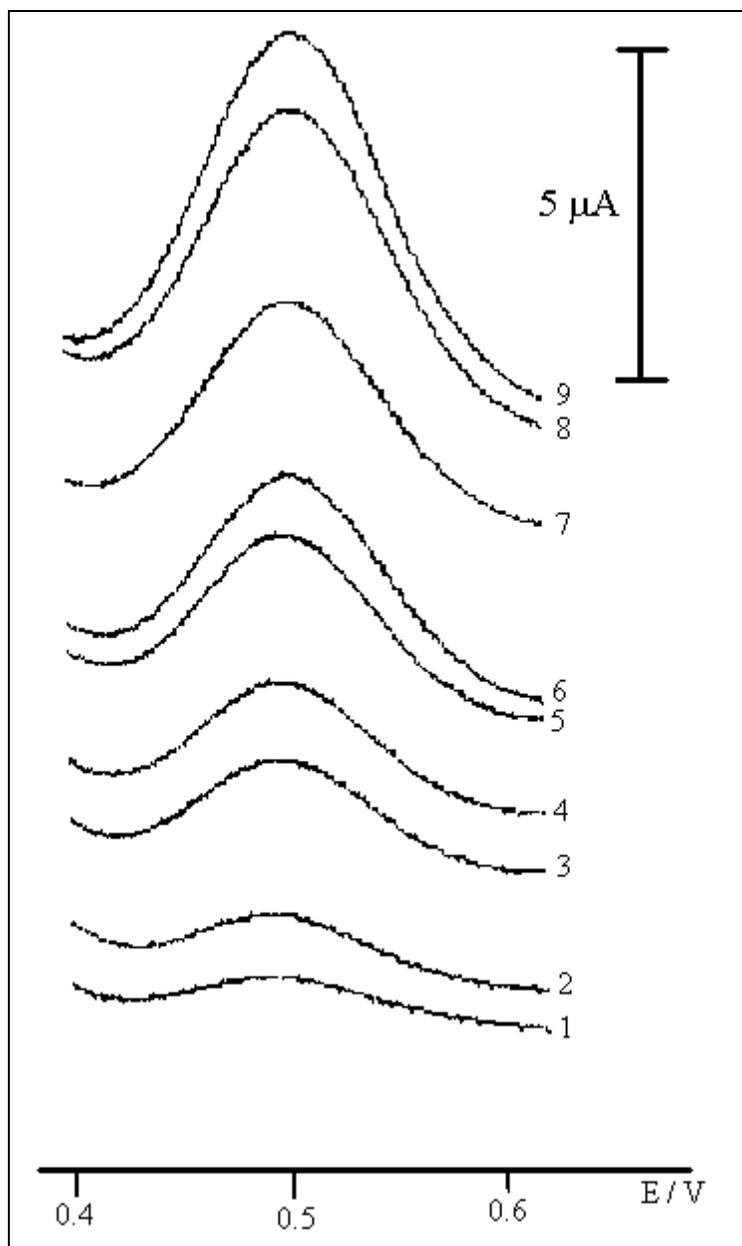


Figure 20: Differential pulse voltammograms of platinum electrode modified with $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ in 0.5 M KCl + Fe^{3+} solutions for 5 min. at -0.30 V. Scan rate = 6.67 mV/s. The solution concentrations are ($\times 10^4$ M): 1: 1.79; 2: 2.51; 3: 3.58; 4: 4.30; 5: 5.37; 6: 6.09; 7: 7.16; 8: 8.95; 9: 10.74.