

Full Paper

Electrochemical Detection of 2-Naphthol at a Glassy Carbon Electrode Modified with Tosflex Film

Ming-Chih Tsai, Po-Yu Chen*

Faculty of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung City 807, Taiwan (R.O.C.)

*e-mail: pyc@kmu.edu.tw

Received: January 15, 2007

Accepted: March 20, 2007

Abstract

In this study, a Tosflex (a perfluoro-anion-exchange membrane) modified glassy carbon electrode has been used to detect 2-naphthalenol (2-naphthol) in aqueous solutions in order to demonstrate the electroanalytical application of Tosflex. 2-naphthol polymerizes upon electrochemical oxidation at a glassy carbon electrode; however, the current related to this oxidation is too small for analytical purpose at low concentration level. A Tosflex polymer modified glassy carbon electrode (TFGCE) was found of having capability to improve the detection limit because 2-naphthol molecules deprotonated in basic solutions to form 2-naphtholate anions that were accumulated to TFGCE by the anion-exchange characteristic of Tosflex. The accumulated 2-naphtholate anions were determined with the following differential pulse voltammetry. With 3 minutes accumulation at +0.05 V, the dependence of oxidation current versus concentration was linear from 8×10^{-7} M to 1×10^{-5} M with a regression coefficient of 0.999 and a detection limit of 2×10^{-7} M. Unlike many other anion-exchange polymer modified electrodes, the TFGCE is stable at highly basic condition.

Keywords: 2-Naphthol, Tosflex, Modified electrode, Anion-exchange, Differential pulse voltammetry

DOI: 10.1002/elan.200703857

1. Introduction

There are many types of modified electrodes developing for electroanalytical tasks including the detection of metal ions and organic compounds [1]. For the electrochemical detection of ion redox analytes, the electrodes modified with a thin film of ion-exchange polymers are very adequate and they are very conveniently and easily fabricated. The presence of ion-exchange film allows the quick preconcentration on the electrode surface and, therefore, enhances the following voltammetric detection limit. Among the various ion-exchange polymers, the perfluorinated polyionic polymers such as Nafion and Tosflex [2] are of particular interest because they demonstrate outstanding stability over a wide pH range. Additionally, they are nonelectroactive over a wide potential range and insoluble in aqueous solutions. However, their slight solubility in alcohols with short carbon chains allows preparing a uniform thin film-coated electrode by a simple method, the spin-coating. A lot of examples corresponding to the Nafion-coated electrodes used for the determination of inorganic and organic cations in aqueous samples have been reported [3]. The anion-exchanging Tosflex-modified electrodes, however, were almost only employed for the determination of metal ions such as Hg(II), Cu(II), Tl(III), Bi(III), Te(IV), and Se(IV) [4–9] as their complex anions. To the best of our knowledge, the applications of Tosflex modified electrode to the

determination of organic anion in aqueous samples are very rare. There is one report published [10].

2-naphthol is widely used in pharmaceutical and dye industries in the production of antirheumatic naproxen and azo-dyes, but on the other hand, it is a toxic compound and its disposal causes remarkable environment pollutions. Actually, waste aqueous solutions containing 2-naphthol are treated by physical and chemical methods [11–14] or electrochemical procedure [15]. The methods employed for the determination of 2-naphthol are relatively rare and its electroactivity supposes that a voltammetric technique should be adequate. In fact, 2-naphthol has been determined electrochemically by measuring the oxidation current of 2-naphthol on a boron-doped diamond (BDD) electrode [16]. Although the surface adsorption and fouling of the electrodes by accumulated detection products were prevented while BDD electrodes were employed, the detection limit is not very acceptable (0.125–0.75 mM).

This article demonstrates the electrochemical behavior of 2-naphthol at a glassy carbon electrode (GCE) and the application of Tosflex film-modified glassy carbon electrode (TFGCE) for the 2-naphthol detection. At 25 °C, 2-naphthol exhibits a pK_a value of 9.51 [17]. Under an alkaline condition, 2-naphthol deprotonizes to release one proton and form anionic species that can be accumulated into the TFGCE by the anion exchange characteristic of Tosflex. A much better detection limit can be achieved.

2. Experimental

2.1. Apparatuses

All electrochemical experiments were performed with a CHI 621A electrochemical analyzer (CH Instruments, Inc.) in conjunction with a Bioanalytical Systems (BAS) model C-2 electrochemical cell. The C-2 cell contains a three-electrode system consisted of a glassy carbon disk electrode (BAS MF-2012, geometric area = 0.071 cm²) with or without a Tosflex thin film, a Ag/AgCl (3 M NaCl) reference electrode (BAS MF-2052), and a platinum spiral counter electrode. The functions of stirring and noble gas bubbling/blanket were included in the cell compartment. Before the experiments were carried out, all glassware were cleaned by soaking in 1:1 (v:v) nitric acid for at least 1 hour and then rinsed with deionized water.

The glassy carbon electrode (GCE) was polished with 0.3 μm diameter alumina powder on a wet polishing cloth to a shiny surface. Afterwards, the GCE was rinsed thoroughly with deionized water and then cleaned ultrasonically in deionized water. These procedures were performed between each experiment.

2.2. Chemicals

The Tosflex polymer sheet denoted IE-SA 48 was obtained from Tosoh Soda, Japan. 2-naphthol (99%) and Sodium hydroxide (99%) were purchased from Merck and Riedel-de Haën, respectively. Cl⁻, ClO₄⁻, NO₃⁻, SO₄²⁻, CO₃²⁻ standard solutions were prepared from their sodium salts and used for interference tests. Solutions of nonionic surfactant polyoxyethylenesorbitan monopalmitate (Tween 40, Sigma), anionic surfactant sodium dodecyl sulfate (SDS, Fluka), and cationic surfactant hexadecyltrimethylammonium bromide (HdMe₃NBr, Fluka) were prepared by dissolution in deionized water and used for interference tests. All chemicals were used as purchased without further purification.

2.3. Preparation of Tosflex Polymer Modified Glassy Carbon Electrode (TFGCE)

The Tosflex coating solution was prepared according to the procedure described in the literature [18]. About 2.5 g of Tosflex polymer was dried under vacuum at 110 °C. Afterwards, this piece of polymer was cut very finely and mixed with 10 ml water isopropanol methanol solution in which the volume proportion of water:isopropanol:methanol equals 1:1:1. This solution was heated to about 70–80 °C under reflux for 50 hours. After cooling, the undissolved polymer residues were separated by centrifugation and a clear yellowish solution was obtained. The concentration of the dissolved polymer was determined gravimetrically from an evaporated portion of the solution. A 1 wt% solution was

prepared by diluting with methanol and used as the coating solution.

The TFGCE was fabricated by spin-coating of 4 μL Tosflex solution at a spin rate of 3000 rpm onto a GCE. A uniform thin film was obtained by evaporating the solvent after 4 minutes of spinning.

2.4. Procedures for Voltammetric Analysis

5 mL of the sample solutions was placed in the electrochemical cell for each voltammetric measurement. The deprotonized 2-naphthol anionic species (2-naphtholate) was preconcentrated into the TFGCE by the anion exchange feature of Tosflex while the solution was stirring. A small positive potential (+0.05 V) was applied to the TFGCE to enhance the accumulation efficiency. After 3 minutes of accumulation, the differential pulse voltammogram (DPV) was recorded by applying a positive scan while the solution was kept steady without stirring. The optimized DPV parameters are: amplitude = 0.05 V, pulse width = 0.05 s, pulse period = 0.2 s.

3. Results and Discussion

3.1. Voltammetric Behavior of 2-Naphthol on Bare GCE and on TFGCE

The chemical structures of 2-naphthol and 2-naphtholate, respectively, are demonstrated in Figure 1. The continuous cyclic voltammograms (CV) of 1 mM 2-naphthol in 0.1 M NaClO₄ solution at a bare GCE are showed in Figure 2. Under the pH (ca. 7.0) of this solution, most of the 2-naphthol molecules (pK_a = 9.51 at 25 °C) should be neutral without carrying negative charges. The electrochemical oxidation of 2-naphthol on a bare GCE started at ca. 0.3 V and a single anodic wave with a peak potential, E_p^a , at ca. 0.75 V was observed. During the reverse scan, no cathodic wave appeared indicating the oxidation of 2-naphthol is irreversible at a GCE. The oxidation current decreased remarkably during the repeat scans is due to the formation of insulated polynaphthol film on the GCE surface.

In order to demonstrate the preconcentration ability of Tosflex film, a 0.01 M NaOH solution was used to substitute for the NaClO₄ solution. Under this alkaline environment, most of the 2-naphthol molecules should dissociate to form 2-naphtholate anions. Therefore, it is theoretically possible to accumulate these anionic species to the GCE surface by

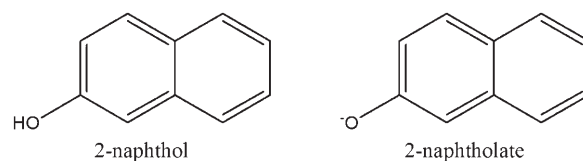


Fig. 1. The chemical structures of 2-naphthol and 2-naphtholate anion.

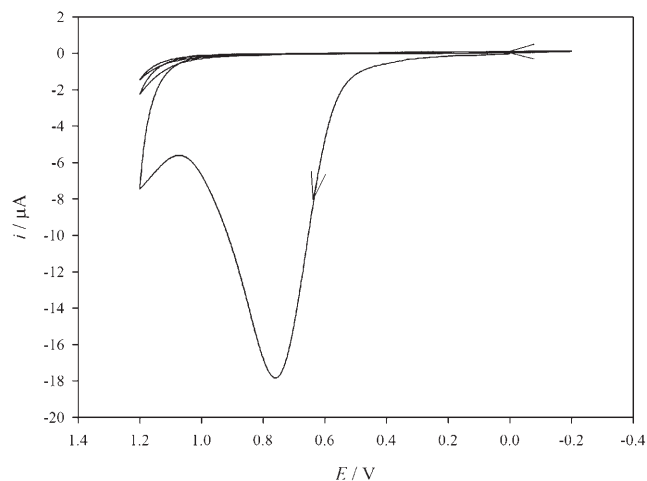


Fig. 2. Continuous staircase cyclic voltammograms of 1 mM 2-naphthol at a bare GCE in 0.1 M NaClO₄ aqueous solution. Scan rate was 100 mV/s. Three scans were recorded.

the Tosflex thin film. Figure 3 represents the linear scan voltammograms (LSV) of 10 μM 2-naphthol in 0.01 M NaOH solution on a GCE with and without the Tosflex thin film, 180 s accumulation was applied before the LSV was recorded. Without the Tosflex polymer coating, no anodic wave appeared indicating the low sensitivity of bare GCE. On the other hand, an obvious anodic wave with a good peak shape appeared while employing TFGCE. This fact indicates that a Tosflex thin film is really capable to preconcentrate 2-naphtholate to the electrode surface and enhance the detection sensitivity. By carefully examining the voltammograms in Figure 3, the peak potential, E_p^a , of 2-naphtholate occurred at a more negative value (ca. 0.45 V) in comparison with 2-naphthol dissolved in NaClO₄ solution. This potential shift might be produced from the alkaline environment because a similar anodic wave was

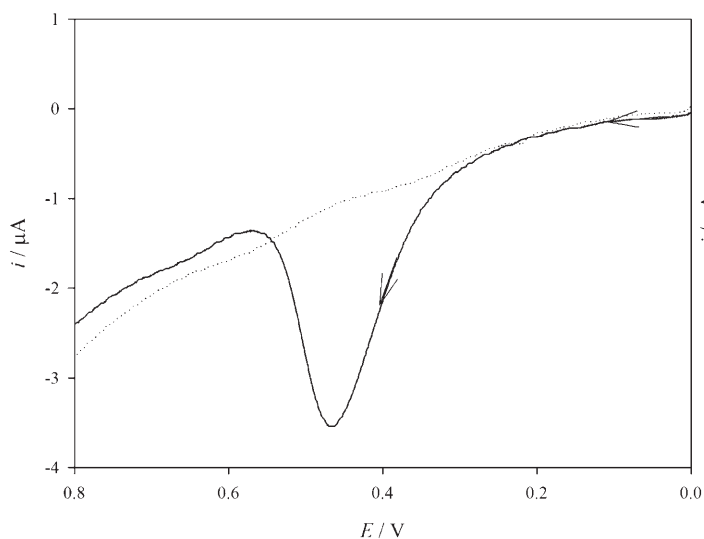


Fig. 3. Linear scan voltammograms of 0.01 M NaOH solution containing 10 μM 2-naphthol at (·····) bare GCE and (—) TFGCE after 180 s accumulation. Scan rate was 100 mV/s.

also observed on a bare GCE in the basic solution with higher 2-naphthol concentration. The oxidation potential of 2-naphtholate ions is more negative than neutral 2-naphthol molecules because anionic species carries higher negative charge density and thus more easily oxidized. Based on the upper observations, an alkaline condition is more favorable for the detection of 2-naphthol at a TFGCE. However, increasing the concentration of NaOH is not beneficial. As can be seen in Figure 4 where the LSV of 10 μM 2-naphthol were recorded on a TFGCE in 0.01, 0.05, and 0.1 M NaOH solutions, respectively. It is obvious that increasing the pH is not necessarily to enhance the detection sensitivity. Actually, a worse sensitivity was obtained in a solution with higher pH value. This phenomenon must result from a competitive interaction between 2-naphtholate ion and hydroxide ion for the limited ion-exchange sites on the Tosflex thin film. Both ions are anions that can be concentrated into the Tosflex thin film by the anion exchange process. In a solution with high pH value, the dominate anions, OH⁻, may have more opportunities to occupy the ion-exchange sites and thus causing a low surface concentration of 2-naphtholate. Based on these observations, the 0.01 M NaOH solution was determined as the medium for the following experiments because a higher sensitivity and an acceptable conductivity could be obtained at the same time.

In order to obtain a well-defined 2-naphtholate oxidation wave and a flatter background current, the differential pulse voltammetry (DPV) was employed in the following experiments.

3.2. Effect of Accumulation Potential

In this study, 10 μM 2-naphthol was detected in 0.01 M NaOH solution using the anodic peak current corresponding to the oxidation of the 2-naphtholate that was accumu-

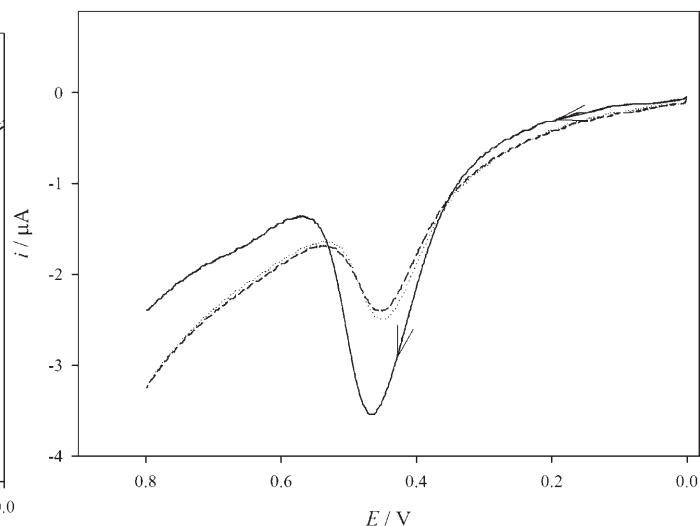


Fig. 4. Linear scan voltammograms of 10 μM 2-naphthol dissolved in (---) 0.1 M, (·····) 0.05 M, and (—) 0.01 M NaOH aqueous solutions at TFGCE after 180 s accumulation. Scan rate was 100 mV/s.

lated on the TFGCE. 2-naphtholate was initially accumulated onto the TFGCE at a proper accumulation potential, E_a , for 3 minutes while the solution was stirred and then the accumulated 2-naphtholate was determined by DPV scanned from -0.2 V to positive direction without stirring. The effect of accumulation potential on the DPV response for 2-naphtholate is illustrated in Figure 5a. As can be seen,

the anodic peak current, i_p , has a maximum value as the accumulation potential is $+0.05$ V. At other values of accumulation potential, the anodic peak current corresponding to the oxidation of accumulated 2-naphtholate is almost unchanged. This behavior is not usual comparing to another example of TFGCE used for the analysis of *O,O*-diethyldithiophosphoric acid [10]. This experiment had

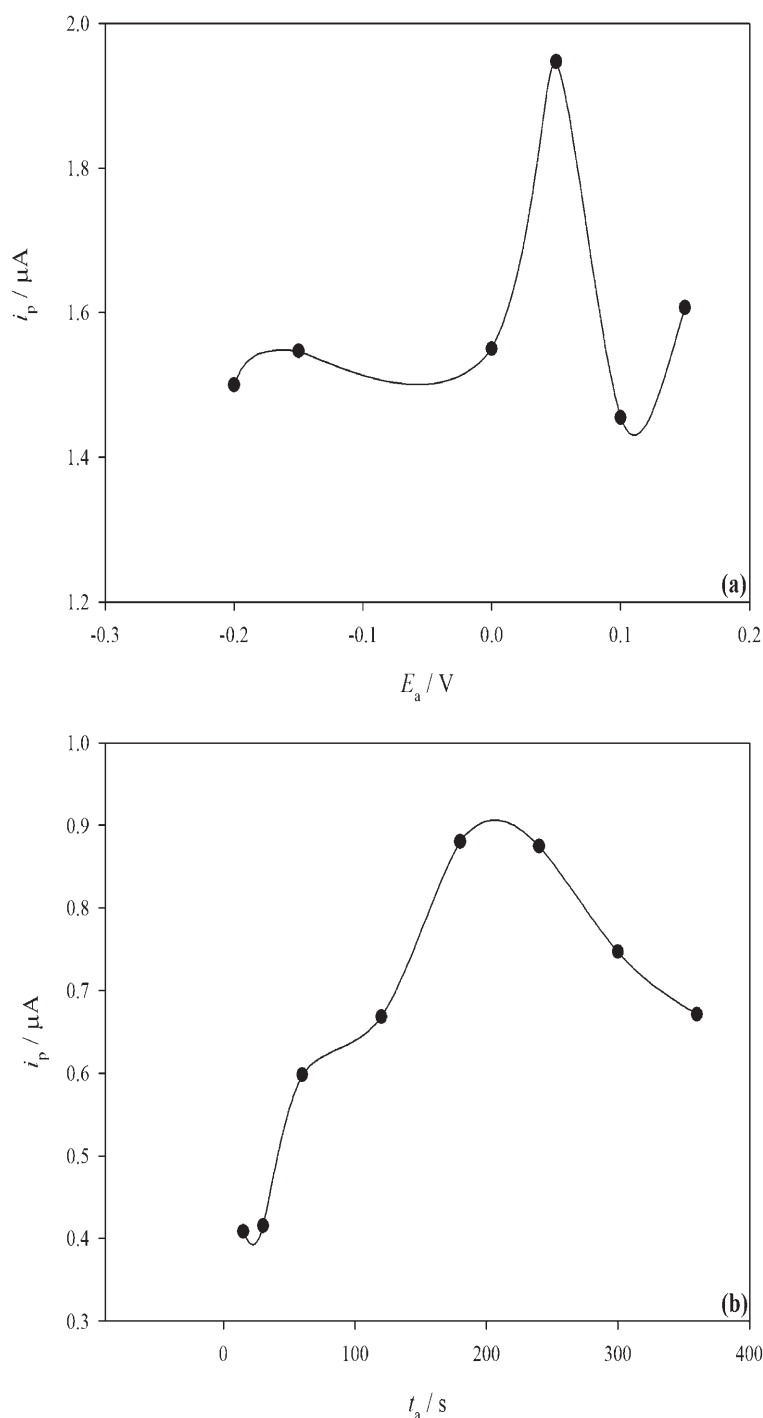


Fig. 5. Effects of a) accumulation potential, E_a , on DPV response for 10 μM 2-naphthol, and b) accumulation time, t_a , on DPV response for 2 μM 2-naphthol, an accumulation potential of $+0.05$ V was applied. DPV parameters: amplitude = 0.05 V, pulse width = 0.05 s, pulse period = 0.2 s.

been repeated for several times and almost identical behavior was obtained. Therefore, the accumulation potential of +0.05 V was chosen for the accumulation step. It is expected that the accumulation of 2-naphtholate is favorable at more positive potential because 2-naphtholate is negatively charged.

3.3. Effect of Accumulation Time

The effect of accumulation time, t_a , on the anodic DPV response of 2-naphtholate was studied in a 0.01 M NaOH solution containing 2 μM 2-naphthol. The accumulation time employed in this study ranged from 15 seconds to 360 seconds. During the accumulation period, an accumulation potential of +0.05 V was applied at the TFGCE. As demonstrated in Figure 5b, the anodic peak current of 2-naphtholate oxidation increases with longer accumulation time and reaches a maximum value while t_a falls in the range between 180 s and 240 s. The 180 s accumulation time was chosen for the following studies based on the consideration of reducing time consumption. The anodic peak current produced from the oxidation of the accumulated 2-naphtholate ions decreased at the accumulation time beyond 240 s. It is still not clear what causes this behavior and more experiments are needed to explain this phenomenon.

3.4. Calibration

For the determination of 2-naphthol, the 0.01 M NaOH aqueous solution was chosen because 2-naphtholate, which is really accumulated through an ion-exchange process onto

the TFGCE, formed in this alkaline environment. OH^- ions would compete with 2-naphtholate ions for the ion-exchange sites on the Tosflex film. Thus, higher concentration of NaOH was prevented but 0.01 M must be used in order to keep reasonable conductivity. This consequence has been discussed in Section 3.1.

2-naphtholate was first accumulated onto a TFGCE at the +0.05 V accumulation potential for 180 s and then anodic differential pulse voltammograms were recorded. A calibration curve was built from the observed anodic peak currents measured individually for 0.8, 1, 2, 4, 6, 10 μM of 2-naphthol. The calibration curve represented in Figure 6 demonstrates a linear behavior between 8×10^{-7} M and 1×10^{-5} M with a slope ($\mu\text{A}/\mu\text{M}$) and a correlation coefficient of 0.2 and 0.999, respectively. The detection limit is 2×10^{-7} M (=0.03 ppm). The inset in Figure 6 represents the differential pulse voltammograms of every standard 2-naphthol samples. The anodic peak current of each sample occurs around +0.45 V. The anodic current at +1.0 V decreased with the increase in 2-naphthol concentration indicating that OH^- ions adsorbed on the ion-exchange sites would be replaced by 2-naphtholate ions at higher concentration of 2-naphthol.

3.5. Interferences

Various inorganic anions and surfactants were examined in respect to their interference with the determination of 2-naphthol since these anions may compete with the 2-naphtholate ions for the limited ion-exchange sites on the Tosflex film and thus influence the accumulation of 2-naphtholate. For 0.01 M NaOH solution containing 6 μM of

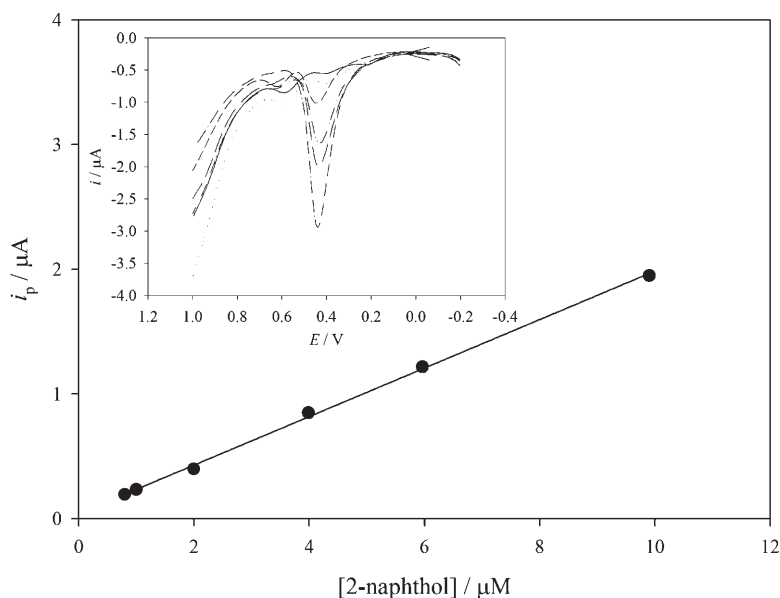


Fig. 6. The calibration curve of 2-naphthol. It was established based on the anodic peak current data taken from the voltammograms showed in the inset in which the standard concentrations of 2-naphthol were 0.8, 1, 2, 4, 6, and 10 μM , respectively. DPV parameters: amplitude = 0.05 V, pulse width = 0.05 s, pulse period = 0.2 s.

Table 1. Interference of inorganic anions and surfactants on the DPV response of 2-naphthol; [2-naphthol] = 6 μM .

Anions or surfactants	Concentration excess over 2-naphthol	Contribution (%) ($i_{p, 2\text{-naphthol}} = 100\%$)
Cl ⁻	1000 \times	-7.98
SO ₄ ²⁻	80 \times	-7.14
ClO ₄ ⁻	40 \times	-4.30
NO ₃ ⁻	10 \times	-11.8
CO ₃ ²⁻	10 \times	-32.7
	1 \times	-28.7
Tween 40	100 \times	-13.6
SDS	10 \times	-70.1
	1 \times	-18.6
HdMe ₃ NBr	20 \times	+12.0

Table 2. Determination of 2-naphthol in tap water and ground water.

	Deionized water	Tap water	Ground water
Detected value, original (μM)	ND	ND	ND
2-Naphthol added (μM)	3.0	4.98	4.98
2-Naphthol found after addition (μM)	2.9 \pm 0.14 [a]	4.71 \pm 0.39 [a]	5.12 \pm 0.40 [a]
Recovery (%)	96.7 \pm 4.7	94.6 \pm 7.8	102.8 \pm 8.0

[a] Average values obtained from 3 detections.

2-naphthol, the results collected in Table 1 show that only chloride ions and nonionic surfactant Tween 40 exhibit lower interference over 100-fold excess concentration. The most serious interferences are carbonate ions and the anionic surfactant SDS. All of the inorganic anions including the anionic surfactant SDS produce a negative deviation indicating that their influence on the determination of 2-naphthol is due to the competition of ion-exchange sites between 2-naphtholate ions and the anionic interferences. The cationic surfactant HdMe₃NBr, however, produced a positive deviation. Although several anionic interferences degrade the performance of TFGCE, the detection of 2-naphthol in real aqueous samples still can be achieved.

3.6. Determination of 2-Naphthol in Water Samples

The analytical application of the procedures for the determination of 2-naphthol was evaluated by applying it to the determination of 2-naphthol in tap water and ground water. Before the experiments were carried out, sufficient quantities of NaOH were introduced into the aqueous samples so that the concentration of NaOH was 0.01 M in each aqueous sample. No 2-naphthol was detected in the original water samples. Both tap water and ground water samples were then spiked with 2-naphthol and their concentrations are showed in Table 2. As can be seen, the recovery of the spiked 2-naphthol is good for both water samples indicating that the effect of interferences in either water sample is almost negligible. In Table 2, the recovery of 2-naphthol has also been carried out in deionized water for comparison.

4. Conclusions

This study reveals that 2-naphthol can be electrochemically oxidized and polymerized at a glassy carbon electrode. However, the anodic peak current is too small to be employed as the analytical signal. Actually, no signal was observed in the 1×10^{-5} M 2-naphthol solution. The sensitivity of detection is significantly enhanced by coating the GCE surface with Tosflex anionic exchange polymer film that exhibits good efficiency of accumulating 2-naphtholate, which is produced from dissolution of 2-naphthol in alkaline solution. Interference may be a serious problem if the water samples contain higher concentration of anions than the 2-naphthol. However, this procedure provide a good and simple method for the determination of 2-naphthol in tap water and ground water samples.

5. Acknowledgements

The authors sincerely acknowledge Prof. Sun in National Cheng Kung University, Taiwan for his kind gift of Tosflex polymer sheet and the financial support of the National Science Council of the Republic of China (Taiwan). (Grant number: NSC 95-2113-M-037-018).

6. References

- [1] J. Wang, *Analytical Electrochemistry*, Wiley, New York **2006**.
- [2] *Tosflex Perfluoro Anion Exchange Membrane, Information Sheet*, Tosoh, Co. Ltd., Tokyo, No. 09588.

- [3] P. Ugo, L. M. Moretto, *Electroanalysis* **1995**, *7*, 1105.
[4] P. Ugo, L. M. Moretto, G. A. Mazzocchin, *Anal. Chim. Acta* **1995**, *305*, 74.
[5] T.-H. Lu, I.-W. Sun, *Electroanalysis* **1998**, *10*, 1052.
[6] H.-Y. Yang, W.-Y. Chen, I.-W. Sun, *Talanta* **1999**, *50*, 977.
[7] H.-Y. Yang, I.-W. Sun, *Electroanalysis* **1999**, *11*, 195.
[8] H.-Y. Yang, I.-W. Sun, *Anal. Chem.* **2000**, *72*, 3476.
[9] M. B. O. Giacomelli, J. B. B. da Silva, A. J. Curtius, *Talanta* **1998**, *47*, 877.
[10] H.-L. Cheng, C.-H. Kuei, I.-W. Sun, *Electroanalysis* **2002**, *14*, 767.
[11] K. Rajeshwar, J. G. Ibanez, G. M. Swain, *J. Appl. Electrochem.* **1994**, *24*, 1077.
[12] Ch. Comninellis, C. Pulgarin, *J. Appl. Electrochem.* **1991**, *21*, 703.
[13] J. D. Rodgers, W. Jedral, N. J. Bunce, *Environ. Sci. Technol.* **1999**, *33*, 1453.
[14] Ch. Comninellis, *Electrochim. Acta* **1994**, *39*, 1857.
[15] M. Panizza, G. Cerisola, *Electrochim. Acta* **2003**, *48*, 1515.
[16] M. Panizza, I. Duo, P. A. Michaud, G. Cerisola, Ch. Comninellis, *Electrochem. Solid State Lett.* **2000**, *3*, 429.
[17] D. R. Lide, *Handbook of Chemistry and Physics*, CRC Press, London **1992–1993**, pp. 8–40.
[18] L. Dunsch, L. Kavan, J. Weber, *J. Electroanal. Chem.* **1990**, *280*, 313.



Saved Search Alerts – Quick and Easy

Simply register. Registration is fast and free to all internet users.

Saved Search Alerts:

You are notified by e-mail whenever content is published online that matches one of your saved searches—complete with direct links to the new material.

To set a Saved Search alert: Run a search on Wiley InterScience, then click

● [Save Search](#) on the results page

Search Results

Show Results in:
[Journals](#) | [Onlinelinks](#) | [Reference Works](#) | [Databases](#) | [Current Protocols](#)

There are 63 results for: 'prions in Article Titles and disease in All Fields, in all subjects product type Journals'

View: 1-25 | 26-50 | 51-63

Select Article Information Sort by: Match % | Title | Product

Fibrillar prion peptide (106-126) and scrapie prion protein hamper phagocytosis in microglia
Gila
Volume 46, Issue 2, Date: 15 April 2004, Pages: 101-115
Janoslava Cieselski-Tredia, Nanoy J. Grant, Gabrielle Ulrich, Matthias Corrette, Yannick Bailly, Anne-Marie Haebler, Sylvette Chazzerat-Golaz, Marie-France Bader
[Abstract](#) | [References](#) | [Full Text](#) | [HTML](#) | [PDF](#) (1919K)

● [Save Search](#)
● [Edit Search](#)

Once you have saved the query, login to "My Profile" and go to **SAVED SEARCHES**.
Click + [Activate Alert](#) to start getting e-mail results for that query.

