

## DETERMINATION OF ORGANOCHLORINE COMPOUND NITROCAPHANUM BY CATHODIC STRIPPING VOLTAMETRY AT NAFION MODIFIED ELECTRODE

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### Abstract

Nitrocaphanum (NC) was determined with detection limit of  $5.5 \times 10^{-9}$  M by cathodic stripping voltametry at Nafion modified electrode. NC response was linear from  $2.2 \times 10^{-8}$  M to  $1.3 \times 10^{-6}$  M. Relative standard deviation of NC detection by this method was 1.7%.

### Introduction

Nitrocaphanum (NC) is an organochlorine compound, which has been proven to be an effective anti-cancer medicine for a number of cancers such as cervix cancer, stomach cancer, lung cancer, breast cancer as well as vicious lymphosarcoma. It is thus important and significant to develop an analytical method for NC determination. At present, the prevalent method of NC determination is spectrophotometric approach (1). Wang and co-workers reported an electroanalytical approach for the determination of some anti-cancer medicines by adsorptive stripping voltametry (2,3). However, to our knowledge, thus far nobody has ever reported the determination of NC by using chemically modified electrode (CME). In this work, determination of NC by cathodic stripping voltametry using Nafion CME is described. The major advantages of NC determination by this method include high sensitivity, wide linear response, good selectivity, and good reproducibility.

### Experimental

#### APPARATUS:

Cyclic voltametry and stripping voltametry were performed with a Model XJP-821 (B) polarographic analyzer (Jiangsu Electroanalytical Instruments Factory) and a Model LM-15 X-Y recorder (Dahua Instruments Factory). All experiments employed a three-electrode cell with a Nafion CME as the working electrode, a platinum electrode and a SCE electrode as the auxiliary and reference electrodes, respectively.

#### REAGENTS AND SOLUTIONS:

NC stock solution ( $1.1 \times 10^{-3}$  M) was prepared by dissolving 20 mg pure NC (Shanghai No. 12 Medicine Factory) with HCl, and then diluting to 50 ml with double distilled water. 0.05% Nafion solution was prepared by diluting 5% Nafion (Aldrich) with methanol.

#### PREPARATION OF NAFION CME:

The modified electrode substrate was a glassy carbon rod sealed into a Teflon cylinder, the exposed electrode surface area is  $7.1 \text{ mm}^2$ . The electrode was first polished by alumina with distilled water as the lubricant, washed ultrasonically with  $\text{HNO}_3$  (1:1) and acetone, successively.

The electrode was then rinsed with distilled water and dried under an IR lamp. The Nafion coating was accomplished by carefully applying 5  $\mu$ l 0.05% Nafion solution to the electrode surface and then drying it under an IR lamp for a few minutes. When methanol was evaporated completely, a Nafion film was firmly attached to the glassy electrode surface.

#### GENERAL PROCEDURES:

Certain amount of NC stock was transferred to electrolysis cell containing pH 2.5 HCl solution, this NC solution was then deaerated with nitrogen for 20 min.. A potential of +0.1 V (vs. SCE) was applied to the Nafion CME while stirring the NC solution. Stop stirring, wait for 30 seconds, then scan cathodically at a scan rate of 100 mV/s. The 1.5th order differential cathodic stripping voltamogram was recorded. A sharp NC reduction peak at -0.59 V (vs. SCE) was observed, which was the basis of NC quantitation.

#### Results and Discussion

##### VOLTAMETRIC BEHAVIOUR OF NC:

Cyclic voltammetry was performed in a pH 2.5 HCl solution containing  $2.2 \times 10^{-5}$  M NC using both glassy carbon electrode and Nafion CME as the working electrodes. It was found that if Nafion CME is employed, a sharp reduction peak at about -0.59 V (vs. SCE) was observed; if glassy carbon electrode is used however, no such peak at all has been observed.

The data obtained in cathodic stripping voltametry agree well with those of cyclic voltametry. As shown in Figure 1, if Nafion CME is used, a sharp stripping peak at -0.59 V is observed in the 1.5th order stripping voltamogram (Curve A), while no such peak is observed if uncoated glassy carbon electrode is used as the working electrode (Curve B).

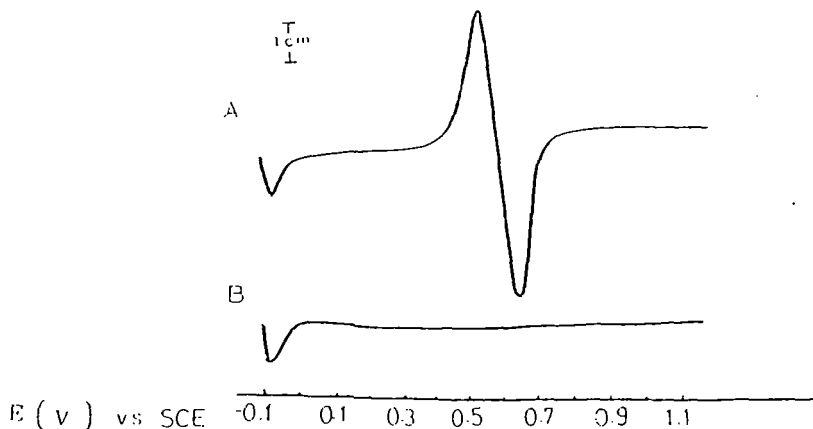
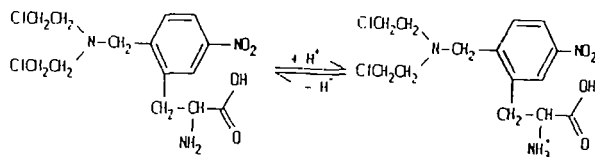


Fig. 1: The 1.5th order differential cathodic stripping voltamogram of Nafion CME (Curve A) and glassy carbon electrode (Curve B) in pH 2.5 HCl solution containing  $2.2 \times 10^{-5}$  M NC.

## ELECTRODE REACTION MECHANISM OF NC:

The enrichment and reaction of NC at Nafion CME could be described as followings:

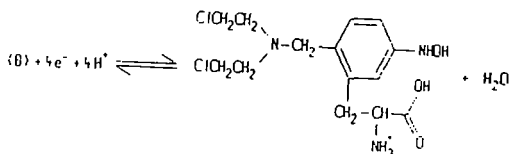
(1). process of protonation



(2). process of enrichment



(3). process of cathodic stripping



(4). process of cleaning



The protonated NC are charge-bearing cations, which possess much larger ion-exchange coefficient with the Nafion film than of neutral NC molecules, thus the NC enrichment can be achieved, as a result, the sensitivity of NC detection can be greatly enhanced.

## OPTIMIZATION OF EXPERIMENTAL CONDITIONS:

- (1) Selection of supporting electrolytes: Same amount of NC was dissolved in 0.01 M HAC, 0.01 M HAC/NaAc, 0.01 M NaCl/HCl, 0.01 HCl and 0.01 M BR buffer solution, respectively. Cathodic stripping analysis was then performed for each NC solution. Although reductive stripping peak was all observed for each NC solution, the highest peak was obtained in 0.01 M HCl medium. Hence, 0.01 M HCl was finally selected for preparing NC solutions.
- (2) Selection of pH values: Six  $1.1 \times 10^{-6}$  M NC/HCl solutions were prepared with pH values range from 1.5 to 4.0. Peak height was then plotted vs. pH value. As shown in Figure 3, the largest current is obtained at pH 2.5. It appears that if the solution is too acidic, the  $\text{H}^+$  or  $\text{H}_3\text{O}^+$  will compete with NC for binding ability of NC to the Nafion film.

- (3) Selection of the thickness of the Nafion film: Six different Nafion CME's were prepared by applying different amount (1  $\mu$ l to 11  $\mu$ l) of 0.05% Nafion solution onto the glassy carbon surfaces. The results indicated that 5  $\mu$ l is the optimum volume (see Fig. 4). It appears that if the Nafion film is too thin, the binding sites for NC are limited. On the other hand, if the Nafion film is too thick, the conductivity of the Nafion may raise a problem.
- (4) Selection of enrichment potential: It was found that from +0.20 V to -0.30 V (vs. SCE), the variation of enrichment potential did not affect the peak height of NC reduction very much. +0.10 V of enrichment potential was finally chosen because at this potential, stable and reproducible NC stripping peaks were obtained.

#### CALIBRATION CURVE AND REPRODUCIBILITY:

After choosing the optimum experimental conditions, the reproducibility of NC determination by this method was examined. For ten parallel NC measurements, the relative standard deviation is 1.7%. The linear range of NC calibration is from  $2.2 \times 10^{-8}$  M to  $1.3 \times 10^{-6}$  M with a detection limit of  $5.5 \times 10^{-9}$  M was achieved.

#### EFFECTS OF COEXISTING IONS:

For a  $1.1 \times 10^{-6}$  M NC solution, 100 times more concentrated  $K^+$ ,  $Na^+$ ,  $Zn^{2+}$ ,  $Ba^{2+}$ ,  $Ca^{2+}$ ,  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Mg^{2+}$ ,  $Ni^{2+}$ ,  $Al^{3+}$ ,  $As^{3+}$ ,  $Fe^{3+}$ , oxalate, citrate, and tartrate have no significant interference toward NC determination. Similarly, 10 times more concentrated  $Cu^{2+}$ ,  $Pb^{2+}$ , and  $Hg^{2+}$  also show no significant interference for NC determination.

#### SAMPLE ANALYSIS:

NC powder and NC injection were obtained from Shanghai No. 12 Medicine Factory. Both NC samples were analyzed by cathodic stripping voltametry with Nafion CME as the working electrode. The NC contents in both samples and the NC recovery rates for both samples are listed in Table 1. The results agree well with those obtained by spectrophotometric method (1).

Table 1: NC Sample Analysis

Sample	Measured NC ( $\times 10^{-7}$ M)	Added NC ( $\times 10^{-7}$ M)	Total NC ( $\times 10^{-7}$ M)	Rate of Recovery (%)	NC Content *	NC Content **
NC Powder	5.60	5.50	11.10	100	98.25%	99.99%
NC Injection	5.50	5.50	11.20	104	20 mg	20 mg

\* measured by cathodic stripping analysis with Nafion CME

\*\* see reference (1) (by spectrophotometric method)

#### References

- (1) Shanghai Medicine Standard 1980, 339.
- (2) J. Wang, P. Tuzhi, M. Lin, T. Tapia, *Talanta* 1986, 33(9), 707.
- (3) J. Wang, M. Lin, V. Viva, *Analyst* 1987, 112(3), 247.