



# Using of anionic adsorption property of a surfactant modified clinoptilolite nano-particles in modification of carbon paste electrode as effective ingredient for determination of anionic ascorbic acid species in presence of cationic dopamine species



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## ABSTRACT

A novel carbon paste electrode containing modified clinoptilolite nano-particles with hexadecyltrimethylammonium surfactant (or surfactant modified zeolite (SMZ)) was constructed and used for selective voltammetric determination of ascorbic acid (AA) in the presence of dopamine (DA), because the SMZ present in the modified electrode adsorbs anionic AA species and repels cationic DA species. This caused to increase the over-voltage of electro-oxidation of DA by  $\sim 600$  mV with respect to AA in square wave voltammetry (SqW). Hence, AA and DA can be effectively determined by the modified electrode in their aqueous mixture. Comprehensive CV, SqW and chronoamperometry (ChA) studies were done on AA using the proposed electrode. The widest linear responses with detection limits of  $6.1 \times 10^{-8}$  mol dm<sup>-3</sup> and  $5.9 \times 10^{-12}$  mol dm<sup>-3</sup> were respectively obtained for AA in SqW and ChA techniques. The diffusion coefficient of ascorbic acid was equal to  $4.1 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>. The proposed method was successfully applied for the determination of AA in different pharmaceutical and food samples which of their AA contents were obtained as:  $497.4 \pm 1.2$  mg per Chewable tablet,  $246.9 \pm 1.4$  mg per Vitamin C tablet,  $501.3 \pm 0.8$  mg per Vitamin C ampoule,  $45.2 \pm 1.1$  mg per 100 g of Sweet lemon,  $50.6 \pm 0.7$  mg per 100 g of Orange,  $36.9 \pm 0.9$  mg per 100 g of Grapefruit,  $31.2 \pm 1.3$  mg per 50 g of Sour lemon,  $9.5 \pm 1.0$  mg per 250 mg of Lemonade.

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## 1. Introduction

Ascorbic acid (AA), one form (“VI tamer”) of vitamin C, is a naturally organic compound plays an important role in body health due to its antioxidant effect [1]. It is a water-soluble vitamin and necessary to metabolism which is essential for reduce of iron, formation of collagen and dissolved oxygen [2,3]. Message transfer in the central nervous system significantly depends on dopamine (DA), so low levels of DA may cause neurological disorders such as schizophrenia and Parkinson’s disease [4].

Different methods have been used for AA determination. Some of used methods such as: spectrophotometry [5], fluorometry [6],

chromatography [7], chemiluminescence [8] have major disadvantages including: high cost, low molecular sensitivity, difficult preparation, background interference (for fluorometry) and destroying of sample and non-repeatability (for chromatography). In recent years electrochemistry methods have paid attention to overcome these problems. But, some modified electrodes have some disadvantages. For example, enzyme based electrodes are non stable [9], polymer based electrodes [10] have good stability but formation of these electrodes is difficult and dye based electrodes [11] are not very good electrodes, because dye degradation environmental. Among chemically modified electrodes, carbon paste electrodes, and the modified one, have important advantages including: ease of preparation and regeneration, stable response and very low Ohmic resistance [12–14]. Due to unique properties of zeolites, they have been widely used for the modification of carbon paste electrodes in recent decades [15,16]. Due to presence of a net permanent negative charge of zeolites they count as good cation exchangers, but by modification

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of them with cationic surfactants such as hexadecyltrimethylammonium (HDTMA) and formation of a surfactant bilayer on the zeolite surface a charge reversal takes place from negative to positive on the resulting modified zeolite. In this case, the surfactant modified zeolite (SMZ) adsorbs anionic species. The construction of SMZs has been illustrated with more details in literature [17–21].

As far as we know, major problem in the electrochemical determination/detection of AA is the coexistence of DA as a biologically important compound. Hence, introducing the suitable modifiers can select one of these compounds (AA or DA) is very important for the electrochemists. As we also know, anionic form of AA is present as major AA species in aqueous solution which can easily adsorb by SMZs. Hence, we prompted that to construct a SMZ-modified carbon paste electrode to increase its selectivity for the voltammetric determination of AA. For this goal, clinoptilolite nano-particles were prepared via ball-mill method and modified with hexadecyltrimethylammonium bromide as a famous cationic surfactant (HDTMA). The obtained SMZ was used as suitable modifier for the modification of carbon paste electrode and finally the proposed electrode was used in the voltammetric determination of AA (in the presence of dopamine). Good results were obtained in the presence of dopamine and determination of AA in different pharmaceutical and food samples.

## 2. Experimental

### 2.1. Reagents and chemicals

Clinoptilolite, belong to the Semnan region in the north-east of Iran, was obtained from Afrand Touska Co. (Isfahan, Iran). Graphite powder, Nujol oil (spectroscopic grade mineral oil), ascorbic acid, hexadecyltrimethyl ammonium bromide, and other analytical grade chemicals were purchased from Merck chemical company and used without further purification. Doubly distilled water was used thorough the experiments. Ascorbic acid solutions were freshly prepared as daily required. Phosphate buffers were prepared from phosphoric acid and sodium hydroxide solution as appropriate. Real samples were diluted with NaCl solution ( $0.1 \text{ mol L}^{-1}$  buffered at pH 6) before running experiments.

### 2.2. Preparations

Natural clinoptilolite was crushed with an agate mortar and sieving in analytical sieves for the separation of micronized

clinoptilolite particles (M-Clino) with mesh –400. M-Clino powder was used for preparation of nano-particles of zeolite using a planetary ball mill under controlled milling conditions such as rotational speed, ball to powder ratio as well as, grinding time, so the crystallinity retained during the size reduction process (dry milling duration 6 h). For removing water soluble and magnetic impurities, the obtained powders were heated at  $70^\circ\text{C}$  in distilled water for 8 h on a magnetic stirrer. This was repeated ( $n=4$ ) to ensure the elimination of voltammetric response of iron at the applied potential ranges for the modified CP electrodes with NClino or MClino. The suspensions were centrifuged and the solid powders air dried.

Typical procedure for the modification of micronized particles and clinoptilolite nano-particles by the surfactant is illustrated at follows: 0.5 g N-Clino was lightly ground and mixed with 20 mL HDTMA-Br solutions at concentration of 0.05, 0.1 and  $0.2 \text{ mol dm}^{-3}$ . The obtained suspensions were shaken on a magnetic stirrer for 24 h and finally centrifuged and the solid materials air dried for 72 h. The resultant NSMZs were assigned as N-SMZ (0.05), N-SMZ (0.1) and N-SMZ (0.2). Similar method was used for modification of micronized clinoptilolite particles (MSMZ).

Typical method for constructing the modified electrode is described below [22]. Adequate amounts of the obtained N-SMZ was mixed with 100 mg graphite powder and Nujol oil was added to obtain the modifier percentages of 10, 20, 25 and 30% W of NSMZ in the CP. After thorough hand mixing in a mortar to obtain a fine paste, a portion of the obtained paste was packed into the end of an insulin syringe (i.d. 2 mm). Electrical contact was made by forcing a copper wire positioned in back of the paste in syringe. This electrode will refer as NSMZ/CPE thorough the text. The modified electrode with micronized particles (MSMZ/CPE), the modified electrode with raw clinoptilolite nanoparticles (NClino/CPE) and HDTMA modified electrode (HDTMA/CPE) were respectively prepared in a similar way by adding of MSMZ, NClino and HDTMA to the carbon paste. Unmodified carbon paste electrode (CPE) was also prepared in the similar method but without adding any modifier. The electrode surface was polished using a soft paper and then rinsed with water.

Preparations of real samples are summarized below:

**Chewable tablet and Vitamin C tablet:** 1 g portion of a finely powdered sample was dissolved in a 100 mL of NaCl solution ( $0.1 \text{ mol dm}^{-3}$  pH 6) and then 25 mL of the prepared solution was transferred to the voltammetric cell.

**Vitamin C ampoule:** 5 mL sample was diluted to 100 mL with NaCl solution ( $0.1 \text{ mol dm}^{-3}$  pH 6) and then 25 mL of the prepared solution was transferred to the voltammetric cell.

**Lemonade:** 20 mL sample was diluted to 100 mL with NaCl solution ( $0.1 \text{ mol dm}^{-3}$  pH 6) and then 25 mL of the prepared solution was transferred to the voltammetric cell.

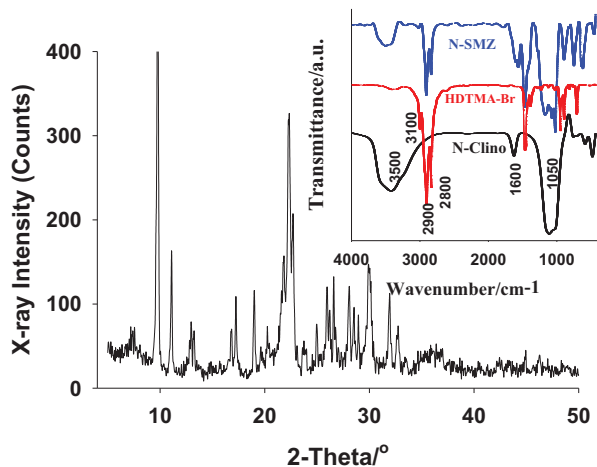
**Orange, sour lemon, grapefruit and sweet lemon:** 100 g of each sample was taken in a mixer. The resultants were filtered to remove un-soluble materials and the filtrate was diluted to 100 mL with NaCl solution ( $0.1 \text{ mol dm}^{-3}$  pH 6) and then 25 mL of the prepared solution was transferred to the voltammetric cell.

**Human serum:** Human serum samples were prepared by the local Hospital Blood Bank. Human serum samples were obtained by centrifugation of Human blood and frozen at  $-20^\circ\text{C}$  until assay. Frozen human serum samples were left on the bench to thaw naturally and were vortex prior to their use.

**Human urine:** Human urine samples were also supplied by a local hospital and used without any sample pretreatment. Both human serum and urine samples were centrifuged (4500 rpm) and diluted properly.

### 2.3. Characterization

The X-ray diffraction pattern of sample was recorded by using a Bruker diffractometer, D8 advance, X-ray tube anode, (Cu  $K\alpha$ )



**Fig. 1.** XRD pattern of NCP; Inset: FT-IR spectra for (a) HDTMA, (b) NCP and (c) SMZ samples.

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