



Electrochemistry-based determination of pungency level of hot peppers using the voltammetry of microparticles



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ABSTRACT

The electrochemical behaviour of capsaicin on a paraffin-impregnated graphite electrode (PIGE) was investigated using square-wave (SWV) and cyclic voltammetry (CV) in a wide range of pH values (2.0–11.0) and potential scan rates. The electrochemical oxidation of capsaicin is an irreversible process and occurs in a complex, pH dependent mechanism. In electrolytes with $2 \leq \text{pH} \leq 10$ oxidation involves the transfer of two electrons and two protons, followed by chemical transformation and the formation of a product which undergoes a further reversible redox reaction. However, at pH close to pK_a the product of two-electron electrochemical oxidation of capsaicin dissolves into the electrolyte.

Analysis of microparticles of dry ground pepper samples immobilized on the surface of PIGE was performed using SWV under optimal experimental conditions of pH 11, pulse amplitude of 50 mV, frequency of 150 Hz, and step potential of 2 mV. The presence of capsaicin in samples was registered with good precision and sensitivity. The proposed methodology exploits the current intensity of capsaicinoids in pepper samples in order to classify samples according to their pungency. A strong positive correlation was observed between the measured peak currents for capsaicinoids in pepper samples and the average of Scoville heat units reported in the literature ($R=91.3\%$).

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1. Introduction

Hot peppers (*Capsicum* spp.) are important vegetables consumed worldwide either fresh or in processed forms (pickled, dried: whole and ground, smoked, in sauces, etc.). They are among the most popular food additives around the world because of their sensory attributes of pungency, aroma and colour. One of the most desirable characteristics of hot peppers from a consumer's point of view is pungency, i.e. the ability to produce an organoleptic sensation of heat. Pungency is caused by capsaicinoids, alkaloids found only in the fruits of hot peppers [1,2]. The most abundant capsaicinoids in hot peppers are capsaicin (8-methyl-N-vanillyl-*trans*-6-nonenamide) and dihydrocapsaicin (8-methyl-N-vanillyl-nonanamide), which are responsible for about 90% of the spiciness. In addition to capsaicin and dihydrocapsaicin, many less abundant capsaicinoids have been detected in hot peppers, including nordihydrocapsaicin, norcapsaicin, homocapsaicin, etc. [3–5].

In addition to food additive uses in our diet, capsaicinoids have drawn considerable interest in recent years due to their multiple biological properties that may affect human health. These include potential chemopreventive and anticarcinogenic effects [6,7], antioxidative activities [8–10], regulation of energy metabolism [11], anti-inflammatory [12], analgesic [13] and antimicrobial properties [14].

As consumer demand for hot peppers increases, the pungency level of hot peppers and their products becomes more important, and an accurate and precise measurement of pungency is necessary. The first method developed to assess the level of pungency of hot peppers or other spicy foods was the Scoville Organoleptic Test [15], which is rather subjective since it relies on the tester's perception of pungency. Therefore, the Scoville test has been replaced with instrumental methods. For determination of total capsaicinoids spectrophotometric methods have been used [16,17]. Separation techniques used for determination of capsaicinoids in hot pepper samples include thin layer chromatography (TLC) [18], gas chromatography (GC) [19] and high-performance liquid chromatography (HPLC). The later technique is the most frequently used one for the analysis of capsaicinoids. HPLC

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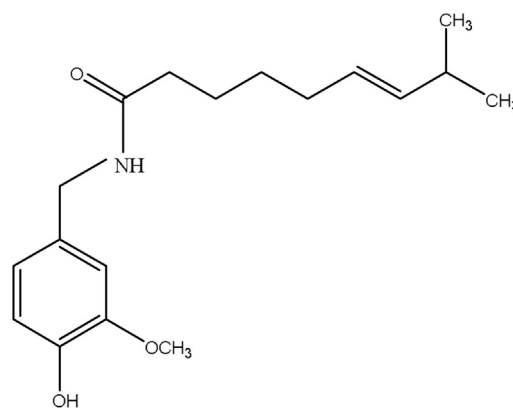
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methods with UV–vis [5] and fluorescence [20–22] detection have been reported for determination of capsaicinoids in fresh and processed hot peppers (powdered peppers, sauces and canned peppers). The only official HPLC method recognized for determination of capsaicinoids is outlined in a manual of the American Spice Trade Association (ASTA) [23]. According to literature, methods using HPLC have limited selectivity and correct identification of individual capsaicinoids solely based on chromatographic behaviour and UV spectrophotometric data is impossible due to a complex matrix and structural similarity between capsaicinoids. Therefore, the most recent methods for determination of capsaicinoids use HPLC coupled to more selective mass spectrometry [24–27]. Chromatographic methods are generally time-consuming, require expensive instruments and complicated sample preparation methods. Thus, there is an interest in developing less expensive and simpler methodologies that could be used for a routine analysis of pepper's pungency.

Electrochemical techniques, particularly voltammetry, are a promising alternative to traditional methods due to their low-cost, good miniaturization potential, as well as rapid and simple analysis. Literature survey reveals several voltammetric methods for determination of capsaicinoids i.e. of the pungency level of peppers and their products. The first investigation was performed by Kachoosangi et al., who developed an adsorptive stripping voltammetric method at a multiwalled carbon nanotube modified basal plane pyrolytic graphite electrode (MWCN-BPPGE) for quantification of capsaicin in a variety of hot pepper sauces [28]. Yardim et al. reported adsorptive stripping voltammetric methods at boron-doped diamond (BDD) [29] and disposable pencil graphite (PG) electrodes [30] for quantification of capsaicin in commercially available dried pepper products. In addition, quantification of capsaicin in hot pepper powders was performed by linear sweep voltammetry on a carbon paste electrode modified with amino-functionalized mesoporous silica (NH₂-FMS/CP) [31]. The most recent electrochemical methods evaluated the application of screen printed carbon nanotube electrodes [32,33] and back-to-back screen-printed sensors (a single walled carbon nanotube back-to-back sensor and a cobalt phthalocyanine mediated bulk modified back-to-back sensor) [34] for detection of capsaicin in real hot peppers and in hot pepper sauces.

All analytical methods for determination of capsaicinoids and pungency levels reported up to date involve solution phase detection, requiring prior dissolution/extraction procedures (see Refs.16–30). The extraction of capsaicinoids from peppers and their products is time-consuming and usually involves the use of organic solvents, which enhances the costs of analysis. In this context, voltammetry of immobilized particles (VIM) offers a great opportunity in developing an easy, simple and fast method for the determination of the pungency level of hot peppers, especially because this technique does not necessitate treatment of sample prior to analysis. The VIM is based on the record of voltammetric response of water-insoluble solid microparticles mechanically immobilized onto the surface of a paraffin-impregnated graphite electrode in contact with aqueous electrolyte [35]. This technique has previously been applied to study various minerals, alloys, and organic compounds [36–38]. It was also used for the direct identification of drugs of abuse [39,40] and estimation of antioxidative activity in tea leaves [41], fruits and vegetables [42].

The aim of the present work is to develop a simple and rapid electrochemical method for the direct determination of hot pepper's pungency in solid samples by voltammetry of immobilized microparticles. The applicability of the method is demonstrated by determining the pungency levels in a variety of commercially available hot pepper powders.



Scheme 1. Chemical structure of capsaicin.

2. Experimental

2.1. Chemicals

Capsaicin ($\geq 95\%$, from *Capsicum sp.*; for chemical structure see Scheme 1) was purchased from Sigma. KNO₃ and buffer solutions pH 2–11 were from Kemika, Zagreb, analytical grade. CaCO₃ was from Merck (suprapur). Water was deionised by Millipore Milli-Q system to the resistivity $\geq 18\text{ M}\Omega\text{ cm}$. The liquid electrolyte was 0.1 M KNO₃ buffered to the particular pH.

2.2. Samples

Nine hot (Bhut Jolokia, Red Savina, Fatalli, Habanero Orange, Carolina Cayenne, Cayenne, Jalapeno, Ancho and Hungarian wax pepper) and two sweet pepper powder samples (ground dried peppers) were purchased from local stores in Croatia. The samples were stored at room temperature and used as received for analysis. The sources of tested samples are listed in the footnotes to Table 1.

2.3. Modified electrode preparation

Voltammetric experiments were performed at modified paraffin-impregnated graphite electrodes (PIGE) (diameter 5 mm, length 50 mm) obtained from Professor Fritz Scholz from Ernst Moritz Arndt Universität Greifswald.

Table 1

Net peak currents and net peak potentials (mean value of six replicates \pm SD) of abrasive square-wave voltammograms of pepper samples on PIGE immersed into 0.1 M KNO₃ at pH 11. Frequency is 150 Hz, pulse amplitude 50 mV and step potential 2 mV.

| pepper | Scoville unit | E_{p1}/V | $\Delta I/\mu A$ |
|-----------------------------------|------------------------|-------------------|--------------------|
| Bhut Jolokia ^a | 880000–1041427 | 0.288 \pm 0.014 | 139.37 \pm 11.25 |
| Red Savina ^b | 350000–577000 | 0.309 \pm 0.015 | 40.28 \pm 7.61 |
| Fatalli ^b | 125000–400000 | 0.326 \pm 0.017 | 74.38 \pm 13.05 |
| Habanero Orange ^b | 150000–325000 | 0.333 \pm 0.012 | 52.55 \pm 9.04 |
| Carolina Cayenne ^c | 100000–125000 | 0.290 \pm 0.020 | 52.06 \pm 6.85 |
| Cayenne ^d | 30000–50000 | 0.282 \pm 0.019 | 15.11 \pm 3.07 |
| Jalapeno ^a | 2500–5000 | 0.288 \pm 0.016 | 5.52 \pm 1.04 |
| Ancho ^a | 1000–2000 ^d | 0.325 \pm 0.018 | 2.13 \pm 0.32 |
| Hungarian wax pepper ^e | 1000–8000 | 0.317 \pm 0.019 | 3.88 \pm 0.76 |
| Sweet pepper ^c | 0 | n.d. | n.d. |
| Sweet pepper ^d | 0 | n.d. | n.d. |

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