Electrochemical Properties of Compounds Present in Saffron

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Abstract
Electrochemical properties of safranal and crocin, which are present in saffron spice, were studied at glassy carbon (GCE) and boron-doped diamond (BDD) electrodes in various organic and aqueous electrolytes. Both compounds exhibited oxidation signals, which can be used for their possible analytical determination. In the case of safranal, the sensitivity of the detection was higher in organic solvents with the addition of $LiClO_4$ than in aqueous electrolytes. More intensive current peaks were obtained at the GCE in acetonitrile than at the BDD. A linear range of 1−300 µmol L^{-1} of safranal was attained at the GCE in organic media.

Keywords: Safranal, Crocin, Glassy carbon electrode, Boron-doped diamond electrode, Saffron.

Introduction
Saffron is a spice derived from the stigmas and styles, called threads, of saffron flowers (*Crocus sativus* L.). They are manually collected and dried for use as a seasoning and coloring agent in food. Due to the labor-intensive manual harvest, saffron is considered the world's costliest spice by weight. Among many compounds present in saffron, some of them are of great importance in assessing the overall quality of the spice in terms of aroma, color, and taste. Safranal (2,6,6-trimethylcyclohexa-1,3-diene-1-carbaldehyde) is an aldehydic aromatic compound that is mainly responsible for the characteristic aroma of saffron spice. It has electroactive properties and can be oxidized at various electrode materials. However, only a few works have been reported concerning the electroanalysis of safranal. Armellini et al. [1] used a glassy carbon electrode for the electrochemical oxidation of safranal together with crocin in the mixture of ethanol and acetonitrile (1:1) with the addition of $LiClO_4$. Yousefi-Nejad et al. [2] described the use of an electronic tongue with four different working electrodes for the classification of saffron quality using cyclic voltammetry of micromolar concentrations of safranal. Heidarbeigi et al. [3] published an application of a portable electronic tongue based on several screen-printed electrodes with different electrode materials and their modifications.

Crocin (8,8-diapo-8,8-carotenoic acid or *trans*-crocetin di-(β-D-gentiobiosyl) ester) is a diester formed from the disaccharide gentiobiose and the dicarboxylic acid crocetin. It is soluble in water and provides the yellow color of saffron. It is also an electroactive compound and can be oxidized, apparently at lower oxidation potentials than in the case of safranal. There are only a few reports on its direct electrochemical detection in aqueous [4] or organic supporting electrolytes [1]. Indirect determination of crocin was also presented [5]. This contribution aims to assess the electrochemical properties of both compounds for their possible electroanalytical determination at glassy carbon (GCE) and boron-doped diamond (BDD) electrodes.

Experimental
Safranal and crocin were analyzed at GCE (diameter 3 mm, Metrohm Czech Republic, Prague, Czech Republic) or printed sensor with boron-doped diamond electrode formed via chemical vapor deposition (working and counter electrode) and Ag/AgCl reference electrode (Slovak Technical University in Bratislava, Bratislava, Slovak Republic). All measurements with GCE were carried out in a three-electrode arrangement with a silver-silver chloride reference electrode containing the

corresponding organic solvent with 0.1 M $LiClO_4$ and a platinum counter electrode. Organic solvents of HPLC grade were acetonitrile (ACN), ethanol (EtOH), dimethyl sulfoxide (DMSO), and dimethylformamide (DMFA) and were bought from various producers. Electrochemical analysis was performed using PGSTAT30 potentiostat/galvanostat and Nova 1.11 software (all Metrohm Czech Republic, Prague, Czech Republic).

Results and Discussion

Safranal is highly soluble in organic and mixed aqueous-organic media, but not in pure aqueous electrolytes. On the contrary, crocin is instantly soluble in aqueous solutions, whereas it is hardly soluble in ACN, moderately in EtOH a soluble in DMSO and DMFA. Such solubility properties might limit the use of some supporting electrolytes. Safranal exhibits an intensive oxidation signal at 1.6 V and a reduction at –1.5 V at GCE in ACN (Fig. 1). BDD shows the same electrochemical response for safranal as at the GCE with very low background currents.

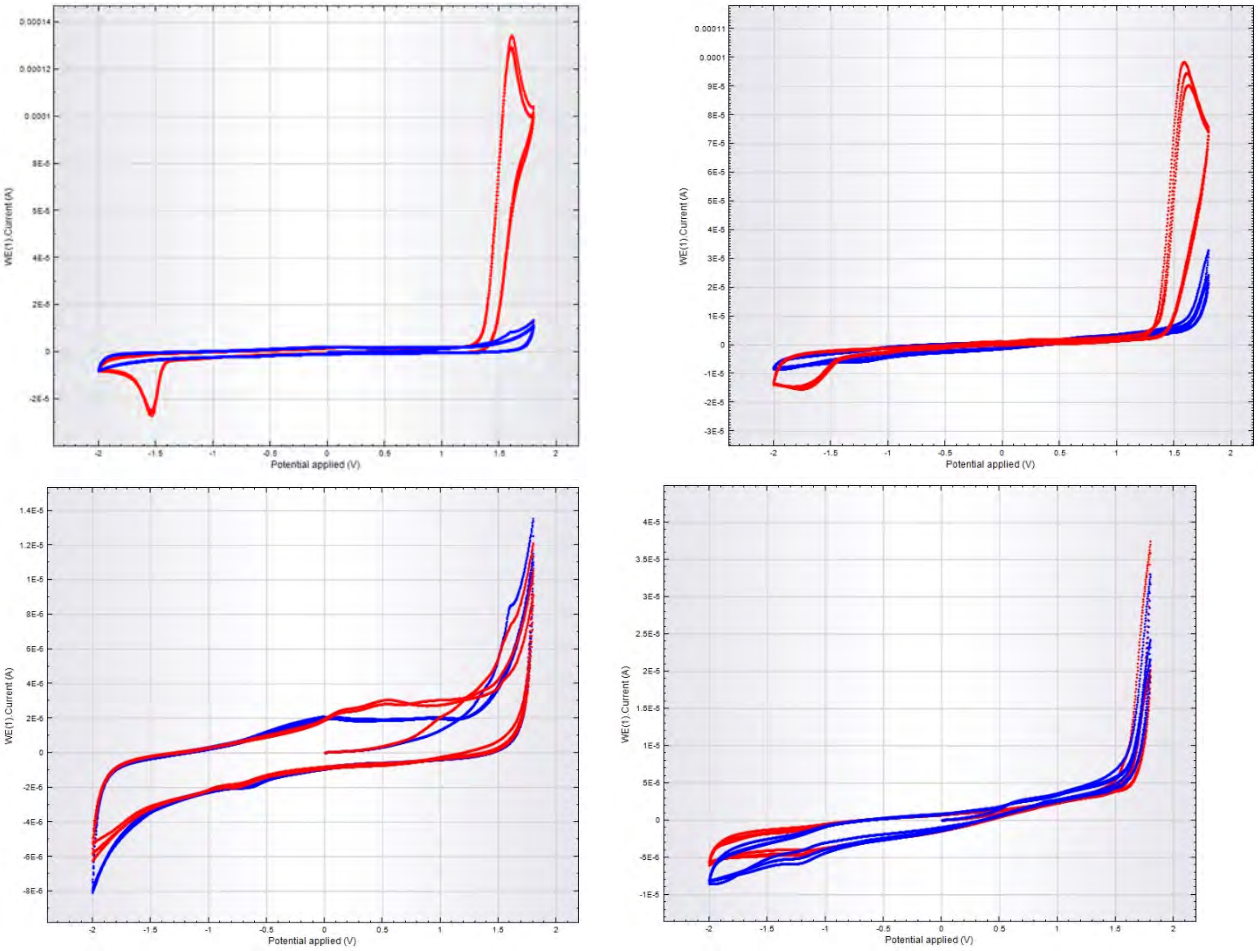

Fig. 1. Cyclic voltammograms of safranal (top) and crocin (bottom) at GCE (left) and BDD (right) electrodes.

Different characteristics were recorded at the GCE in other solvents. In EtOH, oxidation of safranal was shifted to 1.25 V, whereas two reduction signals appeared at –1 V and –1.65 V. Electrochemical oxidation was not visible in DMSO, and two reduction waves similar to those in EtOH were obtained, which were only slightly shifted to more positive potentials. In DMFA, oxidation was not observed in the first scan; only a single reduction peak at –1.65 V emerged. A complex anodic response with several coalesced signals with a maximum of –0.5 V appeared after passing the reduction signal, which remained constant during subsequent scans. The same electrochemical signals in different organic solvents were acquired using a BDD sensor but in overall lower currents. In the case of crocin, an increased oxidation current response with a maximum of 0.5 V was observed at the GCE in ACN, which was shifted to 0.7 and 0.9 V in EtOH and DMFA, respectively. Reduction of crocin was seen only in DMFA at –1.7 V. No redox activity of crocin was recorded in DMSO.

The intensive oxidation of safranal in ACN was further studied. The parameters of differential pulse (DPV) and square wave voltammetry (SWV) were optimized with respect to intensive current peaks and low background currents. The resulting calibration dependencies were linear within the concentration range of 1−300 µmol L^{-1} at both GCE and BDD but with worse analytical performance for BDD. The highest sensitivity was obtained using SWV with parameters optimized for the maximum current response. However, apparent deviation from linearity was observed in this case. The oxidation signal of safranal was stable even after many repetitive scans at the same electrode surface of polished GCE. BDD sensor shows remarkable stability in the detection of safranal, allowing several tens of measurements using only one sensor despite its complicated structure with various printed layers. However, it is necessary to change the sensor after prolonged use due to the slow but continuing degradation of the sensor in organic solvent.

Conclusions

An electrochemical study of safranal and crocin revealed a possibility of their electrochemical detection in organic or mixed aqueous-organic media. The stability of the oxidation signal of safranal at the GCE allows a simple detection without the need to polish the electrode. Moreover, the printed sensor with a boron-doped diamond electrode could also withstand an aggressive environment of organic media to such an extent that the quick calibration with several repetitive measurements of the sample is feasible with one sensor only.

Acknowledgments

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