



Discrimination of apple juice and herbal liqueur brands with solid-state electrodes covered with polyaniline and thiocalixarenes

G.A. Evtugyn^{a,*}, S.V. Belyakova^a, R.V. Shamagsumova^a, A.A. Saveliev^b, A.N. Ivanov^a, E.E. Stoikova^a, N.N. Dolgova^a, I.I. Stoikov^a, I.S. Antipin^a, H.C. Budnikov^a

^a A.M. Butlerov' Chemistry Institute, Kazan State University, 18 Kremlevskaya Street, Kazan 420008, Russian Federation

^b Department of the Modeling of Ecological Systems of Kazan State University, 18 Kremlevskaya Street, Kazan 42008, Russian Federation

ARTICLE INFO

Article history:

Received 29 January 2010

Received in revised form 19 April 2010

Accepted 10 May 2010

Available online 19 May 2010

Keywords:

Solid-contact ion-selective electrode

Thiocalixarene

Principal component analysis

Linear discriminant analysis

ABSTRACT

Solid-contact ion-selective electrodes based on glassy carbon electrode covered with electropolymerized polyaniline and tetrasubstituted thiocalix[4]arene ionophores with hexyl and *o*-pyridylamido functional groups at the lower rim have been developed and examined in the discrimination of the brands of apple juices and herbal liqueurs. For this purpose, the liquids tested were diluted and spiked with a constant amount of Fe³⁺ ions. The variation of the signal toward Fe³⁺ ions was achieved due to their involvement in the reactions with the organic ligands and the antioxidants present. As was shown, the combination of the three electrodes with various receptors makes it possible to predict the brand of apple juices and herbal liqueurs using linear discriminant analysis in 95–100% cases. The discrimination procedure makes it possible to discriminate liquids within 20 min. Besides, the electrodes developed make it possible to detect individual antioxidants (ascorbic, malic, oxalic acids, hydroquinone, and quercetin) in the range from 5.0 × 10⁻⁶ to 1.0 × 10⁻² M in direct potentiometric measurements and redox titration.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Increasing demands for fast and inexpensive methods for the assessment of food quality stimulate intensive development of sensor devices applicable for this purpose [1]. The analysis of volatile substances in foodstuffs with gas sensors and multisensor systems, e.g. electronic noses, makes it possible to detect bacterial spoiling or classify aroma and other qualities of foodstuffs [2–4]. Meanwhile, the analysis of liquids becomes more and more important. In comparison with conventional analytical tools applied for this purpose, e.g. chromatography, IR and UV spectroscopy, sensors have milder demands to labor staff and offer extended opportunities for continuous monitoring as well as semi-quantitative testing.

From 1985 [5], various sensor systems have been developed for food analysis. At first, multisensor systems were based on voltammetric techniques [6–8]. Simultaneously, potentiometric sensor systems also called electronic tongue with conventional and/or specially designed ion-selective electrodes (ISEs) have been developed and successfully applied for food quality assessment [9–11]. Two of them, i.e. taste sensor based on planar electrodes covered with lipid membranes (Taste Sensing System SA 401, Anritsu

Corp. [9]) and liquid and taste analyzer with a set of silicon transistors (α -Astree, Alfa MOS [12]) are commercially available. Photovoltaic cells [13] and SAW sensors [14] were also examined for the characterization of various complex samples. The signals from the sensors with cross-selectivity toward analyte components are commonly processed using various chemometric approaches like pattern recognition like principal component analysis (PCA), linear discriminant analysis (LDA), etc. [15,16]. The efficiency of discrimination of the foodstuffs was proved by comparison of the results obtained with multisensory systems to those of FTIR spectroscopy, HPLC [17] and sensory panel [18].

Solid-contact sensors based on polymeric coatings with immobilized ionophores directly attached to the electrode surface provide some advantages over conventional membrane ISEs with internal filling and a reference electrode. They are easier to manufacture and operate and flexible in the geometry and dimensions of a sensing surface. Thus, a microsensor array of solid-contact sensors was produced by printed circuit board technology on a solid support. Au microdisk transducers were covered with plastic membranes containing plasticizers, conventional ionophores toward some metal cations and inorganic anions and lipophilic salts. The sensor array were tested for the determination of ammonia and some alkali and alkali-earth metals and then used for the discrimination of juices [19] and milk brands [20]. Polyaniline (PANI) covered with a PVC membrane containing ionophores was used in all-solid ISEs for detecting K⁺ [21], Ca²⁺ ions [22] and

* Corresponding author.

E-mail address: Gennady.Evtugyn@ksu.ru (G.A. Evtugyn).