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POTENTIALLY OF A NEW CALIXARENE PHOSPHONIC ACID AS A CHEMORECEPTOR IN CONDUCTOMETRIC SENSORS FOR ARGININE DETECTION IN AGRICULTURAL RAW MATERIALS

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Data on amino acids content in a variety of agricultural raw materials and livestock feed is of a great practical significance for the efficient livestock production. One of such amino acids that may govern the quality of agricultural raw materials and livestock feed is arginine (Arg). It was reported previously that adulterated or low quality materials and feed show the altered levels of Arg within their amino acid profile. From the standpoint of government, producers and importers, it is necessary to have reliable analytical tools to prevent adulterated products to enter the supply chain of the livestock industry. Nowadays analytical methods based on spectrophotometric, fluorometric and chemiluminescent detection, ion-exchange and high performance liquid chromatography, capillary electrophoresis, mass spectrometry and enzymatic assays are widely used for Arg determination. Despite the satisfied criteria of analytical performance, application of the above-mentioned methods for analysis of complex matrices such as agricultural and feed samples is frequently associated with time consuming sample pre-treatment requiring bulky and/or costly equipment and reagents. In contrast, the hybrid methods that harness properties of calixarenes, functionalized with bio-affine groups, and electrochemical detection approaches may overcome the challenges faced by the field. In particular, this research was aimed at studying a potentiality of arginine-sensitive calixarene phosphonic acid for application as a receptor probe in conductometric sensor for Arg detection.

In this work, 25,27-bis(3-methyl sulfide propoxy)calixarene-methylenebisphosphonic acid was first synthesized and then immobilized on the surface of gold interdigitated electrodes of conductometric transducer by chemisorption. The calixarene sample to be used for fabrication of the sensing membrane was dissolved in dimethyl sulfoxide prior to deposition on the electrode surface; during immobilization, a contact time between gold surface and calixarene was 1 h. After immobilization, the unbound or weakly bound molecules of calixarene were removed from the sensitive surface of the sensor by washing in distilled water at vigorous stirring. The sensor performance was further evaluated using electrochemical impedance spectroscopy (EIS) and portable conductometric device in the differential mode of measurements at 10 mV. The following parameters were investigated during the research: dependency of the sensor sensitivity on the calixarene concentration in the membrane, signal reproducibility, operational stability and response time of the sensor in phosphate buffer solution.

The Nyquist plots obtained in the 100 mHz-100 kHz frequency range revealed the increase in the sensor admittance in response to Arg injections that was dependent on the Arg concentration in the measuring cell. The dynamic range of the developed sensor, studied at 5 mM phosphate buffer solution (pH 7.0), was observed up to 12 mM Arg. The response time of the calixarene-based sensor was found to be 60 s. The optimal concentration of calixarene methylenebisphosphonic acid in the sensing membrane was determined to be 12.5 mg/mL. The developed sensor demonstrated sufficient reproducibility of signals to Arg over one working day, its standard deviation was around 5 %.

Use of 25,27-bis(3-methyl sulfide propoxy)calixarene-methylenebisphosphonic acid for development of the arginine-sensitive membrane on the surface of interdigitated gold electrodes showed a possibility of creation of highly stable, easy in fabrication and of a low cost recognition elements in conductometric sensors for Arg determination.