Miniaturized PVC Sensors for Determination of Fe2+, Mn2+ and Zn2+ in Buffalo-Cows' Cervical Mucus Samples

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Abstract : Three polyvinyl chloride membrane sensors were developed for the electrochemical evaluation of ferrous, manganese and zinc ions. The sensors were used for assaying metal ions in cervical mucus (CM) of Egyptian river buffalo-cows (*Bubalus bubalis*) as their levels vary dependent on cyclical hormone variation during different phases of estrus cycle. The presented sensors are based on using ionophores, β-cyclodextrin (β-CD), hydroxypropyl β-cyclodextrin (HP-β-CD) and sulfocalix-4-arene (SCAL) for sensors 1, 2 and 3 for Fe^{2+}, Mn^{2+} and Zn^{2+}, respectively. Dioctyl phthalate (DOP) was used as the plasticizer in a polymeric matrix of polyvinylchloride (PVC). For increasing the selectivity and sensitivity of the sensors, each sensor was enriched with a suitable complexing agent, which enhanced the sensor's response. For sensor 1, β-CD was mixed with bathophenanthroline; for sensor 2, porphyrin was incorporated with HP-β-CD; while for sensor 3, oxine was the used complexing agent with SCAL. Linear responses of 10^{-7}-10^{-2} M with cationic slopes of 53.46, 45.01 and 50.96 over pH range 4-8 were obtained using coated graphite sensors for ferrous, manganese and zinc ionic solutions, respectively. The three sensors were validated, according to the IUPAC guidelines. The obtained results by the presented potentiometric procedures were statistically analyzed and compared with those obtained by atomic absorption spectrophotometric method (AAS). No significant differences for either accuracy or precision were observed between the two techniques. Successful application for the determination of the three studied cations in CM, for the purpose to determine the proper time for artificial insemination (AI) was achieved. The results were compared with those obtained upon analyzing the samples by AAS. Proper detection of estrus and correct time of AI was necessary to maximize the production of buffaloes. In this experiment, 30 multi-parous buffalo-cows were in second to third lactation and weighting 415-530 kg, and were synchronized with OVSynch protocol. Samples were taken in three times around ovulation, on day 8 of OVSynch protocol, on day 9 (20 h before AI) and on day 10 (1 h before AI). Beside analysis of trace elements (Fe^{2+}, Mn^{2+} and Zn^{2+}) in CM using the three sensors, the samples were analyzed for the three cations and also Cu^{2+} by AAS in the CM samples and blood samples. The results obtained were correlated with hormonal analysis of serum samples and ultrasonography for the purpose of determining of the optimum time of AI. The results showed significant differences and powerful correlation with Zn^{2+} composition of CM during heat phase and the ovulation time, indicating that the parameter could be used as a tool to decide optimal time of AI in buffalo-cows.

Keywords : PVC Sensors, buffalo-cows, cyclodextrins, atomic absorption spectrophotometry, artificial insemination, OVSynch protocol