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Title: Electrochemical determination of perchlorate ion by polymeric membrane and coated graphite electrodes based on zinc complexes of macrocyclic ligands

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3 **Electrochemical determination of perchlorate ion by polymeric**  
4 **membrane and coated graphite electrodes based on zinc complexes of**  
5 **macrocyclic ligands**

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13 **Abstract**

14  
15 The electrode characteristics and selectivities of PVC-based perchlorate selective  
16 coated graphite electrode (CGE) and polymeric membrane electrode (PME) incorporating  
17 the synthesized zinc complexes of 6,7:13,14-dibenzo-2,4,9,11-tetramethyl-1,5,8,12-  
18 tetraazacyclotetradecane-1,4,6,8,11,13-hexaene (I<sub>1</sub>) and 6,7:13,14-dibenzo-2,4,9,11-  
19 tetramethyl-1,5,8,12-tetramethylacrylate-1,5,8,12-tetraazacyclotetradecane-6,13-diene  
20 (I<sub>2</sub>) are reported here. Several membranes having different compositions of PVC,  
21 plasticizers, ionic additives and ionophores were fabricated and the best response was  
22 observed for the membrane having composition I<sub>2</sub>: PVC: BA: HTAB in the ratio of 7: 32:  
23 59: 2 (w/w; mg). The response characteristics of PME based on the above mentioned  
24 membrane was also compared with CGE. The electrode exhibits a Nernstian response for  
25 perchlorate ions over wide concentration ranges *i.e.*  $8.3 \times 10^{-7}$  to  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> (with  
26 PME) and  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> (with CGE) and response time of 12 s and 9 s  
27 for PME and CGE respectively. Furthermore, the electrodes generated constant potentials  
28 in the pH range of 3.0-8.0 for PME and 2.5-9.0 for CGE. The high selectivity of CGE for  
29 perchlorate ions permits its use in the determination of perchlorate ions in water and  
30 human urine samples.

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32 **Keywords:** Macrocyclic Zn (II) complex; Perchlorate selective sensor; Coated graphite  
33 electrode; Polymeric membrane electrode; Potentiometry.  
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