Liquid Membrane Electrodes for the Selective Determination of Nicotine in Cigarette Smoke

Saad S. M. Hassan* and Eman M. Elnemma
Department of Chemistry, Faculty of Science, Qatar University, Doha, P.O. Box 2713, Qatar

Five liquid membrane electrode systems responsive to the nicotinium cation are described. These electrodes are based on the use of the ion-association complexes of the nicotinium cation with tetraphenylborate, 5-nitrobarbiturate, flavianate, reineckate and picrolonate counter anions in nitrobenzene solvent as ion-exchange sites. The performance characteristics of these electrodes, evaluated according to IUPAC recommendations, reveal fast, stable and near-Nernstian responses for 10^{-2}–10^{-5} M nicotine over the pH range 3.5–7. Many inorganic and organic cations do not interfere. The direct potentiometric determination of 3 μg ml^{-1}–1.6 mg ml^{-1} of nicotine in aqueous solutions showed an average recovery of 99.5% and a mean standard deviation of 1.2%. The electrodes were also used for monitoring the titration of nicotine with sodium tetraphenylborate, measuring the pK of nicotine and determining nicotine in the smoke from different cigarettes. The results compare favourably with those obtained by the standard gas chromatographic method.

Keywords: *Nicotine electrode; cigarette smoke; tetraphenylborate, 5-nitrobarbiturate, flavianate, reineckate and picrolonate*

Nicotine constitutes about 98% of the total alkaloid fraction in tobacco smoke and 1–8% of the dried tobacco leaves.[1] It has the common property of inducing an initial and transient stimulation, followed by depression and finally paralysis of the autonomic ganglion (*i.e.*, paralysis of neurones situated in and out of the central nervous system which function on the basis of reflex arc). Many reactions and various techniques have been developed for the determination of nicotine. Spectrophotometric,[2,3] turbidimetric,[4] circular dichroism,[5] infrared spectrometric,[6] indirect atomic absorption spectrometric,[7] polarographic[8] and gravimetric[9] methods have been suggested. Visual acidimetric,[10] iodimetric,[11] amperometric,[12] conductimetric[13] and potentiometric[14] titrations have also been described. Few of these methods proved to be selective for nicotine, or free from interference by basic compounds. Methods based on the use of high-performance liquid chromatography (HPLC),[15] gas - liquid chromatography (GLC),[16] radioimmunoassay,[17] enzyme immunoassay[18] and enzyme-linked immunosorbent assay (ELISA) using monoclonal antibodies[19] have been developed for the selective determination of nicotine. These approaches, however, require special instrumentation, reagents, precautions and experience.

The development and applications of ion-selective electrodes continue in exciting and expanding areas of analytical research because these sensors offer the advantages of simple design and operation, reasonable selectivity, fast response, applicability to coloured and turbid solutions and possible interfacing with automated and computerised systems.[20] Few attempts, however, have been made to develop sensitive potentiometric sensors for the determination of nicotine. The only electrode described was based on the use of nicotine - hydrogen tetra(*m*-chlorophenyl)borate as an electroactive material in a liquid membrane.[21]

In this work, the performance characteristics of five electrodes with high sensitivity, good selectivity and fast response for the nicotinium cation were evaluated and used satisfactorily for the direct determination of nicotine in tobacco smoke. These electrodes incorporate the ion-association complexes of the nicotinium cation with tetraphenylborate, 5-nitrobarbiturate, flavianate, reineckate and picrolonate anions as novel electroactive materials for nicotine.

Experimental

Apparatus

Potentiometric measurements were made at 25 ± 2 °C with a Corning digital pH/ion meter (Model 135) using nicotine liquid membrane electrodes in conjunction with an Orion Ag - AgCl double-junction reference electrode (Model 90-02) containing 10% *m/V* KNO_3 in the outer compartment. An Orion combination pH electrode (Model 91-01) was used for pH adjustment. A solid-state Ag - Ag_2S membrane electrode (Orion 94-16) was used for the standardisation of sodium tetraphenylborate with silver nitrate. Conductivities of the nicotine ion-pair complexes in nitrobenzene solution were measured by means of a Tacussel conductivity cell (Type CM 0.05/G) and a Prolabo Type CD 6N conductivity meter.

Reagents

De-ionised, doubly distilled water was used throughout and all chemicals were of analytical-reagent grade unless stated otherwise. The organic solvents were doubly distilled, analytical-reagent grade materials. Nicotine, sodium tetraphenylborate, 5-nitrobarbituric acid, flavianic acid, picrolonic acid and ammonium reineckate were obtained from Sigma (St. Louis, MO, USA) and BDH (Poole, Dorset, UK). A 10^{-2} M nicotine stock solution was prepared by dissolving 1.62 g of pure anhydrous nicotine base in 500 ml of 10^{-1} M HCl. The pH was adjusted to *ca.* 3 and the solution diluted to exactly 1 l. Dilute solutions (10^{-3}–10^{-6} M) were prepared fresh by appropriate dilution and kept in air-tight bottles. A standard 10^{-2} M sodium tetraphenylborate solution was prepared by dissolving 3.422 g in the minimum volume of water followed by filtration and dilution to 1 l. The solution was standardised by potentiometric titration with a standard 10^{-2} M $AgNO_3$ solution using an Ag - Ag_2S membrane electrode for end-point detection.

Nicotine Ion-pair Complexes

A 30-ml aliquot of 10^{-2} M aqueous nicotine hydrochloride solution was mixed and stirred with a 50-ml aliquot of 10^{-2} M

* Present address: Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt.