



# Ion selective electrodes for protonable nitrogen containing analytes: Metallacarboranes as active membrane components



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## ABSTRACT

Ion selective electrodes with simple electroactive membrane components have been prepared for the testing of dopamine, nicotinic acid, nicotinamide, histamine and metformin in aqueous solutions. The electroactive membrane component is the salt made of the protonated targeted analyte and the metallacarborane anion  $[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ . The reason for the good performance of  $[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  is its large capacity to produce weak hydrogen and dihydrogen bonds with the cation and the plasticizer that prevents leakage of the electroactive component. In this paper, we prove how easy is to produce a sensing material for a specific target. The only requirement is that the target has a protonable nitrogen, a situation encountered in many biological molecules or in many bio-relevant molecules. The analytical parameters for evaluation of ISEs performances, such as linearity range, slope, limit of detection, response time, and selectivity were studied and determined and all the produced selective ISEs have given favorable answer. The proposed electrodes showed Nernstian responses for protonable nitrogen containing analytes for almost 4 decades of concentrations,  $1.00 \times 10^{-6}$  to  $1.00 \times 10^{-2}$  mol dm<sup>-3</sup>, with fast response time (5 s) and adequate operational lifetime (50 days). For Dopamine the prepared ISEs exhibited linear responses with slope of ca. 58 mV decade<sup>-1</sup> within the range  $5.00 \times 10^{-6}$  to  $1.00 \times 10^{-2}$  mol dm<sup>-3</sup> and with a low detection limit of 1 μmol dm<sup>-3</sup>. The limits of detection ranged from 0.7 μmol dm<sup>-3</sup> for nicotinamide up to 6 μmol dm<sup>-3</sup> for metformin.

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## 1. Introduction

In the last decades many methods have been developed for the determination of nitrogen containing compounds in different types of matrices. The disadvantage of these methods was that they required a long sample pre-treatment and also expensive read-out laboratory equipment [1–10]. Therefore, it is important to develop methods that provide accurate results, in a faster, simpler and cheaper routine for the determination of bioactive nitrogen containing compounds. Furthermore, the new test should be suitable for different sample systems from several application fields such as food processing, biochemistry, pharmaceuticals and in clinical analysis. In general, sensors have a broad field of applications in pharmaceutical, clinical and environmental quality control due to their low cost, fast response time and because they are easy to prepare. It is known from the literature that most of the compounds that take part in biochemical reactions are electro-active.

Measuring their concentration is an important task in clinical diagnosis as well as in different areas of experimental life sciences. Dopamine (DA) is an important catecholamine neurotransmitter distributed abundantly in the mammalian central nervous system having a key role in a proper functioning of central nervous, renal, hormonal and cardio vascular systems [11]. Several analytical methods reported earlier for these nitrogen bioactive compounds are based on chromatographic methods using different detection systems leading to time consuming and expensive procedures.

Electroanalytical techniques represent an interesting alternative to chromatographic methods, especially for pharmaceutical analysis due to moderate cost, and apparatus simplicity [12]. In general, in electrochemical studies, the selectivity and the sensitivity of the experiment are improved mostly by an accurate choice of the working electrodes. Dopamine has also been determined from pharmaceutical formulation by electrochemical methods, in particular differential pulse voltammetry and square wave voltammetry using different types of working electrodes such as hanging mercury drop electrode (HMDE) [13], carbon paste electrodes (CPE) [14], glassy carbon electrode (GCE) [15], multi-walled carbon nanotubes (MWCNT) [16], and nanogold indium tin oxide (NGITO) [17].

Ion selective electrodes (ISE) are simple and inexpensive analytical tools, with a fast response-time, a wide dynamic range, easy

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preparation and are simple to use in the experimental procedure. ISEs have therefore been used in the above mentioned application fields for the determination of inorganic and organic compounds in various matrices. Since the pioneering work of Bloch, Simon and Thomas on polyvinyl chloride, PVC based membranes; ISEs have experienced an enormous progress in the last decades [18–20]. Pesavento [21] proposed for DA, ISEs based on graphite screen printed electrodes modified with a multilayer of multiwall carbon nanotubes.

The performance of potentiometric analysis has been improved continuously with respect to the limit of detection and also the selectivity by controlling the ion fluxes through the ion-selective membrane [22,23]. ISEs are therefore an efficient method from an economical point of view and, more importantly, provide a fast and accurate detection of clinical relevant parameters with an excellent sensitivity and selectivity, improving the patient safety in modern daily hospital routines. So, various studies concerning ISEs in medicinal drug determination were performed earlier [24].

In our studies on ISEs based on PVC membranes,  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  was applied as electroactive ion-pair generator and we reported the first potentiometric plastic-membrane sensors for the detection of antibiotics for tuberculosis [25] in complex matrices. Also, we reported pioneering work on the potentiometric detection of amino acid enantiomers without the utilization of chiral macrocycles [26]. In these studies we proposed ISEs based on solid membranes and we demonstrated that ion-pair complexes,  $[\text{cation-NH}]^{n+}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]_n^-$ , incorporated in PVC membranes, are suitable to determine bioactive nitrogen containing compounds  $[\text{cation-NH}]^+$  [25,26].

In this study, our work has been focused in the development of ISEs based on simple and low cost polymer membranes with the aim to determine different bioactive nitrogen containing compounds, such as dopamine, nicotinic acid, nicotinamide, histamine and metformin.

## 2. Experimental procedures

### 2.1. Reagents

All reagents utilized (HCl, Diethylether) were of analytical grade and used without further purification steps. Cesium Cobaltabisdicarbollide,  $\text{Cs}[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ , was purchased from Katchem. High molecular-weight poly(vinyl chloride) (PVC), *o*-nitro phenyl octyl ether (NPOE), di-octyl phthalate (DOP), bis (2-ethyl hexyl) phthalate and dibutyl sebacate were purchased from Sigma–Aldrich, tetrahydrofuran (THF) from Merck, Dopamine (DA), nicotinic acid (NA), nicotinamide (NAmd), histamine (His) and metformin (Met) from Sigma–Aldrich. Solutions of lower concentrations were freshly prepared, by dilution steps with deionized water.

### 2.2. Instrumentation

IR spectra ( $\nu$ ,  $\text{cm}^{-1}$ ; KBr pellets) were obtained on a Shimadzu FTIR-8300 spectrophotometer. The infrared spectra were registered in a KBr pellet using a spectrophotometer SHIMADZU FTIR-8300, which covers a wavelength range from 4000 to  $400\text{ cm}^{-1}$ . The number of scans was 10 and base line correction was also made. The  $^1\text{H}$  and  $^1\text{H}\{^{11}\text{B}\}$  NMR (300.13 MHz),  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.47 MHz),  $^{11}\text{B}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR (96.29 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in  $d_6$ -acetone at  $22^\circ\text{C}$ . The  $^{11}\text{B}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR shifts were referenced to external  $\text{BF}_3\cdot\text{OEt}_2$ , while the  $^1\text{H}$ ,  $^1\text{H}\{^{11}\text{B}\}$ , and  $^{13}\text{C}\{^1\text{H}\}$  NMR shifts were referenced to  $\text{SiMe}_4$ . Chemical shifts are reported

in units of parts per million downfield from reference, and all coupling constants in Hz. The mass spectra were recorded in both, negative and positive ion modes using a Bruker Biflex MALDI-TOF-MS [ $\text{N}_2$  laser;  $\lambda_{\text{exc}}$  337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)].

For the potentiometric measurements a Crison microph 2000 pH/millivoltmeter and a Ag/AgCl,  $\text{KCl}_{\text{sat}}$  as reference electrode were used.

### 2.3. Procedures

#### 2.3.1. Complex preparation

Synthesis of  $[\text{cation-NH}]^{n+}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]_n^-$ ,  $\text{H}^+[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  was obtained from  $\text{Cs}[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$  (0.300 g) and HCl 1 M (15 mL), extracting the resulting solution with diethyl ether (20 mL). The organic layer was shaken three times with HCl 1 M (15 mL  $3\times$ ). Finally, the ether was stripped off and the residue was diluted with water to generate one 0.01 M solution of  $\text{H}^+[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  (solution 1). The targeted analyte to be measured was dissolved in water and enough HCl 3 M to prepare a solution with a concentration 0.01 M (solution 2). Next, the ion-pair  $[\text{cation-NH}]^{n+}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]_n^-$  was prepared by mixing 10 mL of solution 1 with 10 mL of solution 2. After stirring, a yellow precipitate was obtained. This precipitate was filtered off and washed with a solution of HCl 0.1 M and dried in vacuum at 0.1 Torr. This general procedure was applied for dopamine, nicotinic acid, nicotinamide, histamine and metformin.

#### 2.3.2. Electro active $[\text{cation-NH}]^{n+}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]_n^-$ ion-pair characterization

The chemical composition of the generated salts was studied by NMR ( $^1\text{H}$ ,  $^1\text{H}\{^{11}\text{B}\}$ ,  $^{11}\text{B}$ ,  $^{11}\text{B}\{^1\text{H}\}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ), FTIR and MALDI-TOF-MS spectroscopies.

As a result, the following compounds could be identified [HDA]  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ , [HNA]  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ , [HNAm]  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ ,  $[\text{H}_2\text{Met}][\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$  and  $[\text{H}_2\text{His}][\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ . The FT-IR of these salts evidenced dihydrogen bonding, in which were participating B–Hs and  $\text{C}_{\text{cluster}}\text{--H}$  and  $\text{C}_{\text{aryl}}\text{--H}$ .

The spectroscopic details of the ion-pair complexes between  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  and the protonated forms of dopamine, nicotinamide, nicotinic acid, histamine and metformin are presented in Supplementary material.

#### 2.3.3. Electrode preparation

The ion selective electrodes consist in electrode body, a coated copper wire for electrical contact, and the electroactive membrane deposited on the bottom part of electrode made from graphite with epoxy resin. The described ISEs for bioactive nitrogen containing compounds are based on solid membranes consisting of the inert polymer matrix (PVC), the plasticizer (either *o*-nitro phenyl octyl ether (NPOE), or di-octyl phthalate (DOP), or bis (2-ethyl hexyl) phthalate or dibutyl sebacate) and the ion pair complex  $[\text{cation-NH}]^{n+}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]_n^-$  itself. Different compositions of the ISEs membranes were obtained by dissolving different percentage (3% or 7%) (w/w) of the ion pair complex, under permanent stirring, in the plasticizer (63%, w/w). Powder PVC (34%, w/w or 30%, w/w) is dispersed in a defined volume of THF until a viscous but clear solution is obtained. These two solutions are then mixed under stirring until homogeneity is reached. This disperse solution is deposited on the surface of the electrode body and the solvent is evaporated at ambient temperature for 48 h. The deposition of the mixture on electrode was made for all electrodes in the same manner to be able to have a control of membrane reproducibility. The electrodes were prepared and assembled as previously described [27] and they

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