

## A new simple method for the preparation of urea and oxalate ion selective electrode-its preparation and analytical application

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(Acceptance Date 28th May, 2010)

### Abstract

A heterogeneous precipitate has been as ion carriers for the preparation of urea and oxalic acid selective membrane sensor. The electrodes give near-Nernstian response in the linear concentration range of 1M to  $1 \times 10^{-4}$  M with detection limits of the orders of  $10^{-4}$  M. The stable potentiometric signals are obtained with in a short time period of 3 seconds. The effect of pH and the effect of medium have been studied, found to give a better responses selectivity coefficient values

(  $\log K_{\text{urea}}^{\text{pot}}$  ) and (  $\log K_{\text{oxalic acid}}^{\text{pot}}$  ) evaluated using fixed interference method. The sensors have also been used as urea determination in fertilizers.

*Key words:* Urea, Oxalic acid, heterogeneous precipitate, selective membrane sensors.

### Introduction

Urea is a safe vehicle for the body to transport and excrete excess nitrogen. The handling of urea by the kidneys is a vital part of human metabolism. Besides its role as carrier of waste nitrogen, urea also plays a role in the countercurrent exchange system of the nephrons, that allows for reabsorption of water and critical ions from the excreted

urine. This transport of urea is important to prevent the loss of water, to maintain blood pressure, and to maintain a suitable concentration of sodium ions in the blood plasma<sup>1</sup>.

Oxalic acid is used in the restoration of old wood. Its main applications include cleaning or bleaching. important reagent in lanthanide chemistry. Prolonged handling of aqueous solutions cause joint pains<sup>2</sup>.

Direct potentiometric measurements provides a rapid and convenient method for determining the activity of various cations and anions. The technique requires only a comparison of the potential developed in a cell containing the indicator electrode in the analyte solution with its potential when immersed in One or more standard solution of known analyte concentration<sup>3</sup>.

The field of Ion Selective Electrodes (ISEs) bridges fundamental host guest chemistry, membrane science and its specific applications. Because of their simplicity, low cost, sufficiently reliable and respectable measurements, ISEs are recognized as novel analytical tools for selective determination of analyte ions.<sup>4,5</sup>

In the present study, a simple heterogeneous precipitate based membrane have been prepared along with the potentiometric performance of these sensor, effect of pH, effect of medium, response time and selectivity coefficient with respect to different interfering ions have been studied.

**Experimental process:**

*Preparation of Urea Oxalate membrane ion selective electrode :*

10ml of saturated Urea solution (LR Grade, Reachem Laboratory Chem Pvt. Ltd) was mixed with 10ml of saturated Oxalic acid solution (LR Grade, E. merck India Ltd.). A white precipitate was obtained. It was filtered and dried in air for 12 hours and powdered. About 0.2g of powdered precipitate was thoroughly mixed with Araldite (Huntsman advanced materials, India Pvt. Ltd) and the paste was applied on Whatmann filter paper No. 42. This was spread uniformly over the filter paper to obtain 0.9mm thickness of the electro active materials with matrix. This was left in air to dry for 24 hours to get an electro active membrane. A circular piece of this membrane was cut and fixed with resin at one end of the hollow glass tube (diameter 2cm and length 10cm). This tube was filled with saturated solution of urea and reference copper metal wire was inserted (diameter 0.5mm & length 12cm) through other end of the tube in such a way that it remains dipped in saturated solution of urea already filled in this glass tube. This complete assembly will work as an ion selective electrode of urea. This ion selective electrode was kept in 1M solution of urea for one week.

The entire electrode system for the measurement can be represented as

Internal reference	Internal reference	Ion	Sample	External
Electrode	solution - Urea	selective	solution	reference
Cu (Cu wire)	solution	membrane		electrode (SCE)

## Results and Discussion

### Electrode Response:

The Electrode was first conditioned in 1M solution of urea and oxalic acid till it attained stable equilibrium after which it was used for the determination of characteristic study of the electrode. The electrode potential for a series of standard solution of urea and oxalic acid concentration range of 1M to  $1 \times 10^{-4}$  M (Tables 1 and 2) These urea and oxalic acid ISE reveals near Nernstian slopes.

Table 1. Electrode Response- Urea

Concentration of urea solution (M)	E.M.F (volts)
1	0.010
$1 \times 10^{-1}$	0.017
$1 \times 10^{-2}$	0.023
$1 \times 10^{-3}$	0.029
$1 \times 10^{-4}$	0.035
$1 \times 10^{-5}$	0.035

Table 2. Electrode Response – Oxalic acid

Concentration of oxalic acidsolution (M)	E.M.F (volts)
1	0.052
$1 \times 10^{-1}$	0.049
$1 \times 10^{-2}$	0.044
$1 \times 10^{-3}$	0.041
$1 \times 10^{-4}$	0.035
$1 \times 10^{-5}$	0.035

Standard electrode potential of this electrode ( $E^0$ ) determined by extrapolation

method was found to be 0.070V of urea and 0.057V of oxalic acid solution. The Nernstian slope value was found to  $1.3 \times 10^{-3}$  mV/decade of urea solution and  $0.9 \times 10^{-3}$  mV/decade of oxalic acid solution. To find the response time the electrode was dipped in 1M solution of urea and oxalic acid and suddenly the concentration of the solution was changed to 0.1M. The variation in potential was noted at every second till a constant potential was obtained at 3 seconds and remains constants (Graph-I and II)

### Effect of pH:

The influence of pH on the potential response of the electrode was studied at 1M urea and Oxalic acid solution concentration over a pH range of 7-10.11 of urea solution and 4 - 10.11 of oxalic acid solution. The pH was adjusted by using buffer solution. The potential is independent of the pH in the range of 7-10.11 of urea solution and 4 - 10.11 of oxalic acid solution. Hence, this pH range may be chosen as the working pH range of the electrode assembly.

### Effect of partially non-aqueous medium on the working of urea and oxalic acid electrode:

The proposed sensor was investigated in partially non-aqueous media using ethanol and iso -propanol mixture with water. A standard solution containing 1M urea and Oxalic acid in a series of 25%, 50% and 75% ethanol and iso -propanol was added. It was found that the potential remains unaffected in the presence of a series of various percentage of ethanol and iso -propanol (25%, 50% and 75%).

*Selectivity:*

The selectivity, which is an important characteristics of a membrane sensor. It is measured in terms of potentiometric selectivity  $K$ ; it measures the response of the sensor towards the primary ion in the presence of secondary ion present in the sample solution. The selectivity coefficient has been determined by using fixed interference method (FIM) based on semi empirical Nicolski-Eisenman equation. In this method the concentration of primary ion urea and Oxalic acid is varied where as the concentration of secondary interfering ion is kept constant in the test solution which is  $1 \times 10^{-1}$  M concentration of interfering ion in the present case. The potentiometer selectivity coefficient data of sensors for various interfering ions (cations and anions) given in table III, IV, V and VI.

Table 3. Interference by Anions-  
(Urea Solution)

Anions (Interfering ion)	Electrode $K_{\text{urea}}^{\text{pot}}, \text{M}$
F <sup>-</sup>	0.011
Cl <sup>-</sup>	0.015
Br <sup>-</sup>	0.020
I <sup>-</sup>	0.021
SO <sub>4</sub> <sup>2-</sup>	0.02
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	30.023

Table 4. Interference by Cations -  
(Urea Solution)

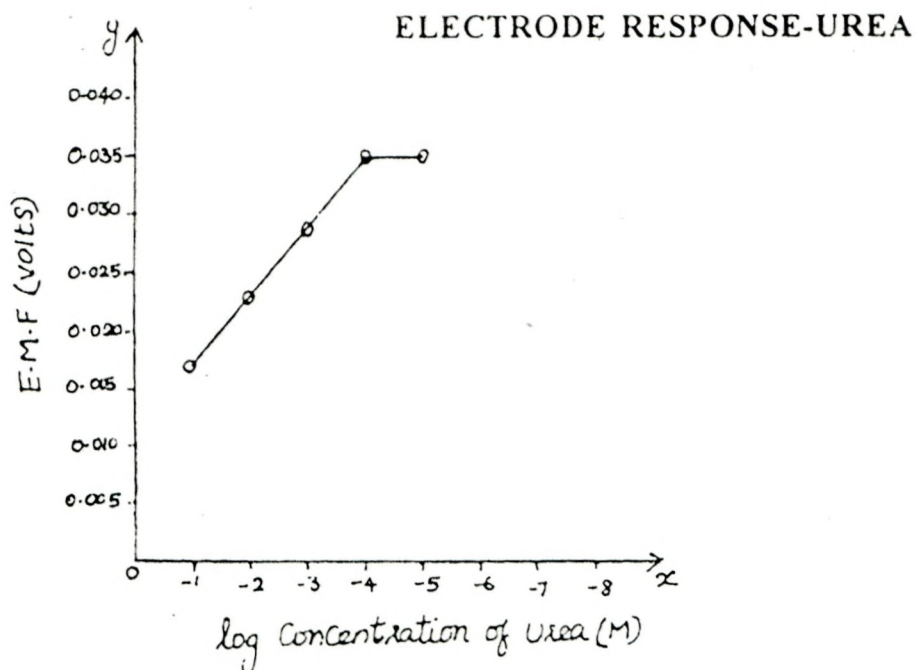
Cations (Interfering ion)	Electrode $K_{\text{urea}}^{\text{pot}}, \text{M}$
K <sup>+</sup>	0.017
Na <sup>+</sup>	0.020
Mn <sup>2+</sup>	0.020
Mg <sup>2+</sup>	0.021
NH <sub>4</sub> <sup>+</sup>	0.025
Cu <sup>2+</sup>	0.026
Ni <sup>2+</sup>	0.027

Table 5. Interference by Anions--  
(Oxalic acid)

Anions (Interfering ion)	Electrode $K_{\text{oxalic acid}}^{\text{pot}}, \text{M}$
Cl <sup>-</sup>	0.044
Br <sup>-</sup>	0.049
I <sup>-</sup>	0.050
SO <sub>4</sub> <sup>2-</sup>	0.051

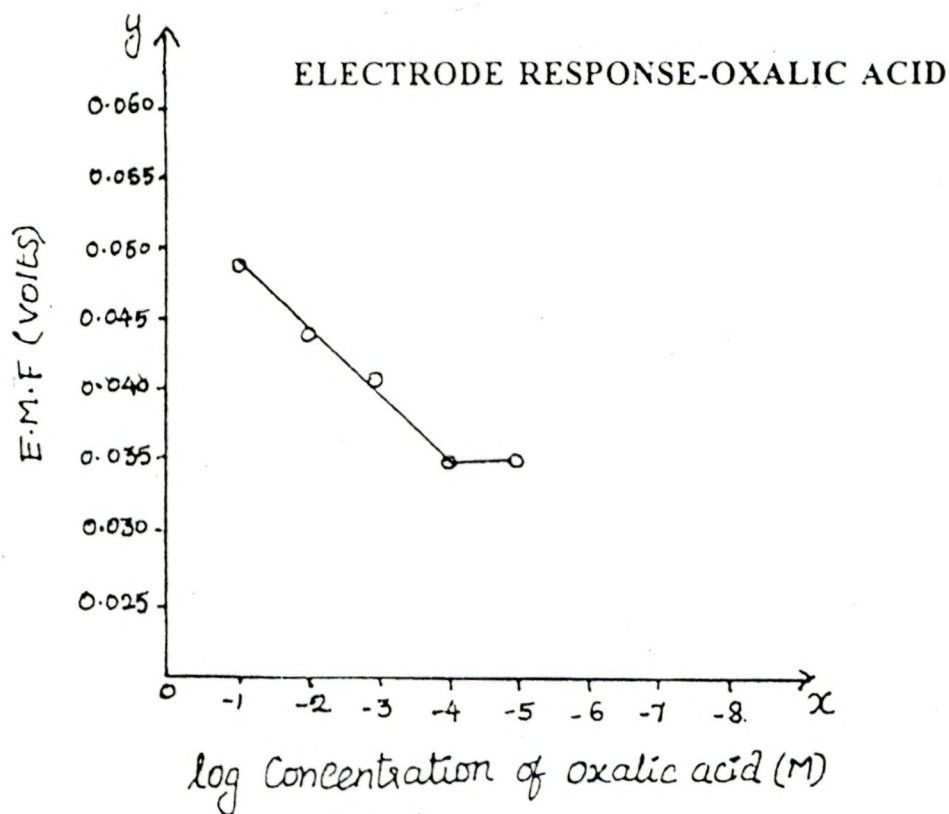
Table 6. Interference by Cations -  
(Oxalic acid)

Cations (Interfering ion)	Electrode $K_{\text{oxalic acid}}^{\text{pot}}, \text{M}$
K <sup>+</sup>	0.035
Na <sup>+</sup>	0.037
Mn <sup>2+</sup>	0.040
Mg <sup>2+</sup>	0.041
NH <sub>4</sub> <sup>+</sup>	0.040



Graph-I

Plot of cell E.M.F (volts) versus log concentration of urea (M)



Graph-II

Plot of cell E.M.F (volts) versus log concentration of oxalic acid (M)

*Analytical Application :*

To assess the applicability of the sensor to real samples, an attempt was made to determine urea in real samples like soil and fertilizers. The recovery of urea in sample analysis was formed to be quantitative with the maximum recovery of 90%.

**References**

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