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Effect of Precipitating Media on the Response Behaviour of Ni(II) Ion-Selective Electrode

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Abstract
Ni(II) being a toxic heavy metal and an environmental pollutant, its monitoring is a matter of great interest to researchers. Among various methods to monitor nickel in environment, Ion-Selective Electrode is currently on rise due its low cost, simplicity and reliability for onsite measurement. This study introduces a new method for the preparation of Ni(II) ion-selective electrode by co-precipitating NiS and Ag_2S in strong alkaline medium in 1:2 mass ratio (NiA1). The results have been compared with the sensor prepared by traditional simple co-precipitation method (NiS1), which has been reported to be not suitable method. The prepared Ni-ISEs are characterized for its phase and morphology by using X-ray diffractometer and scanning electron microscope. Potentiometric characterization has been done with respect to pH stability, Nernstian response, and potentiometric titration. The results show new method as good alternative for preparing Ni(II) ion-selective electrode and NiA1 performs better than NiS1.

Keywords: Ni(II)-Ion selective Electrode, Potentiometric titration, co-precipitation methods, environmental monitoring, pH stability, Nernstian response

1. Introduction
Toxicity of nickel ion is well known and its monitoring has been the subject of great interest. Nickel is abundant in our surroundings due to decomposition or degradation of rocks and soil, biological cycles and especially industrial processes, and water disposal [1, 2]. Environment monitoring of Ni^{2+} is important because it is discharged as pollutants in environments. Monitoring of Ni^{2+} is a challenge as its standard EPA value is 0.03 ppm in drinking water [3-5]. Inhalation of Ni^{2+} beyond its EPA value causes toxic effect in the respiratory tract and immune system. Its adverse effects in human being cause sensitization dermatitis and high concentration of its fume cause respiratory irritant [4]. A review on toxico-kinetics of nickel is available that explains sources of nickel in the environment and its effect on living organisms [5]. Detection and quantification of nickel in our environment is an essential task. There are different methods to detect and quantify metallic nickel in environment which includes sophisticated instrumental methods such as induced couple plasma (ICP), Atomic Absorption spectra (AAS), Flame photometry (FP), Anodic stripping voltammetry (ASV) among others. These methods are expensive and require adequate expertise to handle such instruments. Therefore, ion-selective electrode is considered as better alternative due to its low cost, simplicity, reliability, and can be easily fabricated in laboratory. But, preparation methods for sensing material for Ni-ISE are patented.

First nickel-selective electrode was reported by Pungor and co-workers using a nickel-dimethyl glyoxime complex for the determination of Ni^{2+} ion in aqueous solution[6]. In addition to solid membrane ion selective electrodes (ISE's), liquid membrane electrodes for nickel using O, O'– di isobutyl di- thiophosphato nickel (II) in chloro-benzene, bis (tetraethyl ammonium) bis (di thiobenzophenazine) nickelate in nitrobenzene and nickel diethyldithiocarbamate in chloroform has also been reported [7]. Maharjan had reported on the preparation and characterization of Ni^{2+} ion selective electrode with 2:1 molar ratio of NiS to Ag_2S by simple co-precipitation method [8]. Timilsina had studied the effect of different back contacts with 2:1 molar ratio of NiS to Ag_2S membrane solid contact nickel ion selective electrode prepared by simple co-precipitation method [9]. Heijne et al. have done extensive work on the preparation methods of metal sulfide based solid state ion-selective electrodes [10]. A comprehensive review is given by Buck on the choice of precipitating medium and its effect on the formability of membrane and response of the electrodes towards respective primary ions[11]. It has been stated that alkaline medium does not produce good ion-selective electrodes
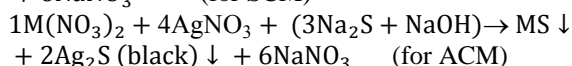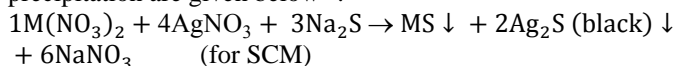
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due its difficulty in forming a membrane that leaks and also it favors the formation of oxide and hydroxides in addition to the formation of sulfides. Therefore, this study aims to propose a strong alkaline medium as precipitating medium for the fabrication of Ni^{2+} ion-selective electrodes and test the response behavior of the resulting sensor.

Materials and methods
Precipitation of NiS
1:2 mass ratio (33.3%Ni: 66.7%Ag) of Nickle nitrate (Qualigens) and silver nitrate (Fisher Scientific) was mixed in a beaker and slowly poured into the beaker containing slight excess of sodium sulphides (Qualigens) to obtain the co-precipitates of NiS and Ag_2S. The above process is called simple co-precipitation method. However, for co-precipitation in strong alkaline medium, 1M NaOH was used as supporting electrolyte for sodium sulfide. This mixture solution was heated up at 50 ºC to 60 ºC in a magnetic stirrer (Staurt Scientific) for one hour to get the complete precipitation. The black precipitate was filtered off by 4g sinter glass crucible and washed several times with distilled water till free from sulfide and metal ions. Finally, precipitate was washed with nitric acid. The precipitate was dried at 100 ºC to 110 ºC in a hot air oven for 24 hour and grounded to very fine powder. This powder was again filtered in 45 micron sieve to obtain finest powder. Possible reactions for both types of co-precipitation are given below[13]:

$$1M(NO_3)_2 + 4AgNO_3 + 3Na_2S \rightarrow MS \downarrow + 2Ag_2S \text{ (black)} \downarrow + 6NaNO_3 \quad \text{(for SCM)}$$

$$1M(NO_3)_2 + 4AgNO_3 + (3Na_2S + NaOH) \rightarrow MS \downarrow + 2Ag_2S \text{ (black)} \downarrow + 6NaNO_3 \quad \text{(for ACM)}$$

The powdery co-precipitate was pelleted and housed into a polypropylene body by silver back contact as reported in our previous work[14-16].

Preparation of solutions
All the stock solutions of 1 M $Ni(NO_3)_2$, 5 M $NaNO_3$, 1 M $AgNO_3$, 1 M EDTA were prepared in doubled distilled water from AR grade chemicals without further treatment. For daily experiment, fresh solutions in the concentration range of 10^{-1} to 10^{-6} M were prepared by serial dilution from stock solution.

Physical Characterization of the membrane
The bulk resistance of the pelleted membrane was measured by using 4-probe method as described elsewhere [17, 18]. X-Ray diffraction measurement was taken with X' Pert MPD-OEC, Phillips X-ray diffractometer, with Cu-Kα radiation at 40 kV and 40 mA. SEM image was taken with KEYENCE REAL 3D system SP Scanning Electron Microscope (SEM) with VE-series 9800 under vacuum condition.

Response Characterization of Ni-ISE
The response of thus fabricated Ni-ISEs was tested in varying concentration of Ni^{2+} ion using $Ni(NO_3)_2$ as test solutions containing 0.1 M $NaNO_3$ as ionic strength adjustment buffer (ISAB). Similarly, the effect of pH on the stability of measured potential was checked by varying the pH from 1 to 10 and potentiometric titration of Ni^{2+} ion using Ni-ISE was carried out against standard solution of EDTA to check if it is suitable for using as indicator electrode in potentiometric titration. Methanol and ascorbic acid were added to $Ni(NO_3)_2$ solution to study the effect of electrolyte composition. The cell configuration for potentiometric experiments is:

$Pt(Hg)/Hg_2Cl_2$, KCl (sat) // test solution $Ni(NO_3)_2$ / Ni-ISE(NIS-Ag_2S)

The potential response of the sensor with Ni^{2+} ion concentration should follow the equation:

$$E_{(Ni)} = E_{(const)} + \log [Ni^{2+}]$$

Results and Discussion
Resistance measurement
Surface resistance of the pellet of active materials for sensor was measured by four-point probe. The measured resistances of the membranes are $3.00 \times 10^1 \Omega$ and $3.97 \times 10^2 \Omega$, respectively for NiS1 and NIA1 pellet. These values of resistance are low value so it does not require the use of high impedance voltmeter to read the cell Emf.

XRD pattern
X-ray diffraction pattern is shown in Fig. 1. From the JCPDS database, presence of binary phase of NiS (JCPDS data card no.75-0613 for Hexagonal system) and Ag_2S (JCPDS data card no.14-0072 for Monoclinic system) existing as a separate phase are confirmed. The peaks for NiS appeared at two-theta values of 34.70(002), 37.88(220), that for Ag_2S appeared at 29.01(111), 30.93(111) and. 31.70(101). Membrane of NiS1 also shows peak of metallic nickel (JCPDS data card no-04-1258) at two-theta of 20.05(111). Presence of metallic particles has been reported to enhance the electrical conductivity of the sensor membrane[19]. XRD pattern confirms the purity and polycrystalline nature of the co-precipitate. There is no ternary phase and no other impurities such as oxides and hydroxides.
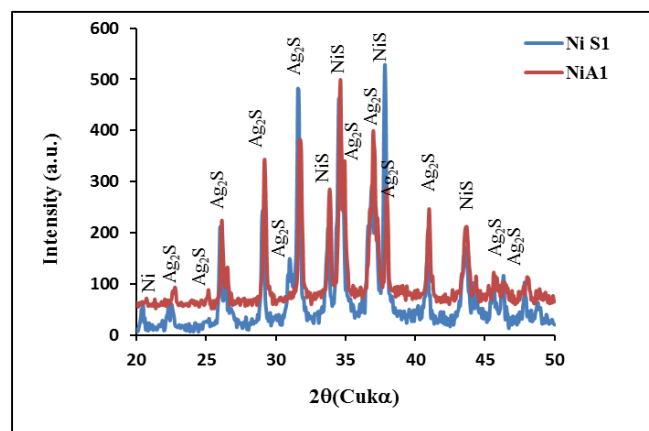

Fig 1: X Ray Diffraction pattern of pellet of Ni-ISEs

Surface morphology with SEM
Surface morphologies of NiS1 (Fig. 2a) and NiA1 (Fig. 2b) samples were examined under scanning electron microscope before polishing the surface and their morphological differences are compared. The sample prepared by simple co-precipitation method (NiS1) is dominated by big fractures. Such surface features are seldom used for sensors as it leads to leakage of soltuion. Similar observation was made my Heijne et al. [11] for CuS pelleting. This could be one of the reasons that since 1977 there has been very limited study on the preparation of metal sulphide based ion senosrs by co-precipitation method. Therefore alkaline co-precipitation method can be considered as superior alternatives method for the preparation of heavy metal ion sensor by respective metal sulphides co-precipiated with silver sulphide. The crakcs were

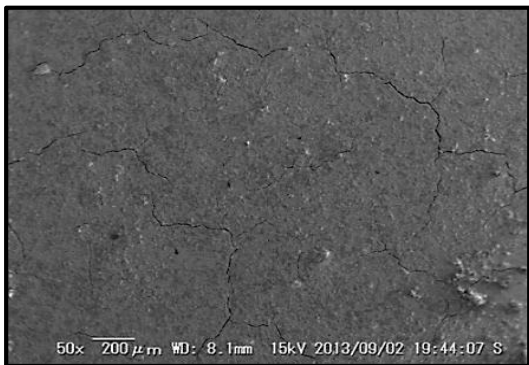removed by polishing the pellet surface and no leakage was noticed.

Fig 2a: SEM images of non-polished surfaces of NiS1

Fig 2b: SEM images of non-polished surfaces of NiA1

pH response

The effects of pH on the stability of membrane potential of both the types of Ni-ISEs are shown in Fig. 3. A constant potential region in NiS1 sensor membrane is obtained over pH 3-8, and from pH 2-9 in the case of NiA1, where the drift of potential was less than ±2mV. The potential of the electrode shows large change either in positive or negative direction when the pH is less than 2 and more than 7. The shift of potential to positive direction is due to adsorption of hydrogen ion on the membrane surface when the pH is lower than 2. Maharjan et al has made similar observation for 2:1 NiS-ISE [9]. There is no possibility of membrane dissolution considering the stability of NiS in Paurbaix diagram [20]. The shift of potential to negative direction at pH higher than 7 clearly shows the precipitation of hydroxide.
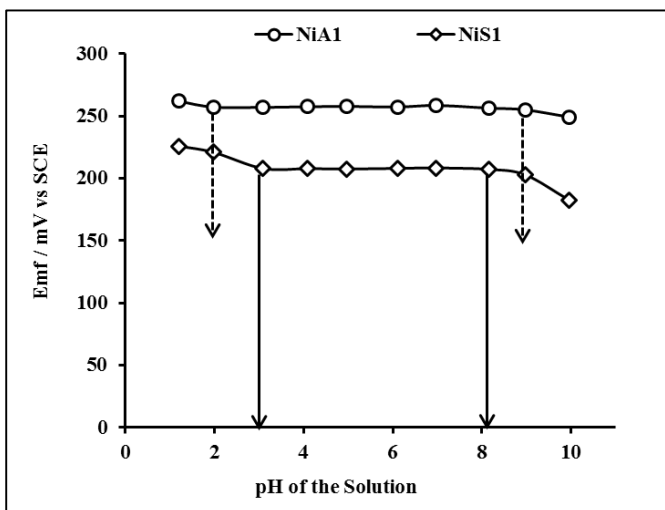

Fig 3: *Comparison of pH response of two Ni^{2+} ISE*

Nernstian Response

Direct potentiometry technique was applied to measure Nernstian response. Nickel nitrate, sodium nitrate, methanol and ascorbic acid at pH 5 were used as electrolyte in three different measurements as shown in Figs. 4. The details about linearity, Nernstian slope and effect of different electrolyte are given in table 1.
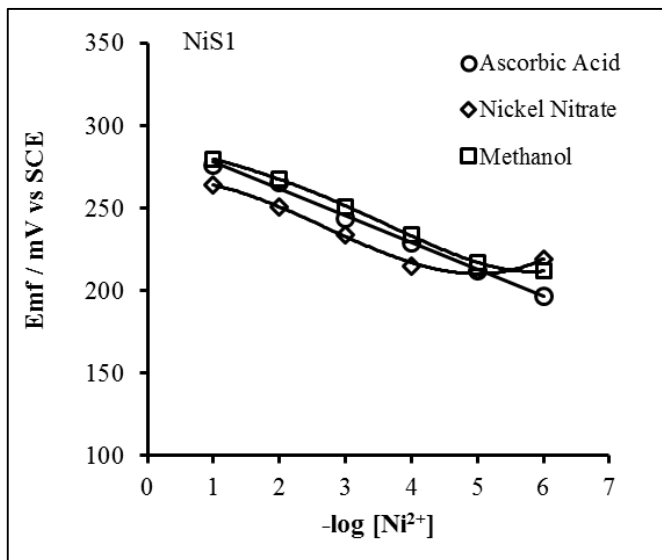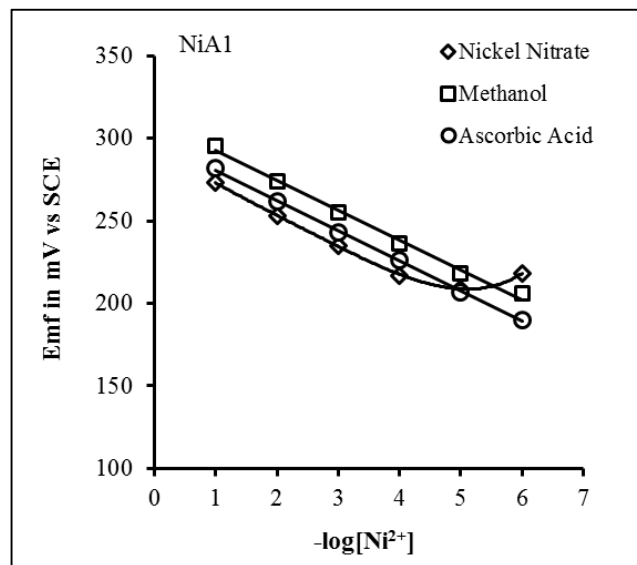

Fig 4a: Nernstian response of NiS1-ISE

Fig 4b: Nernstian response of NiA1-ISE

The results clearly shows superiority of alkaline co-precipitation method as it gives better linearity and Nernstian slope compared to electrode prepared by simple co-precipitation method. NiS1-ISE shows deviation from linearity at higher concentration (0.1M) and it also shows lower detection limit at 10^{-5} M compared to 10^{-6} M for NiA1-ISE. Addition of ascorbic acid in test solution is beneficial in lowering the potential and hence lowering the detection limit by increasing the linearity region in both NiS1 and NiA1-ISEs.

Table 1: Nernstian properties of NiS1-ISE and NIA1-ISE

Sample name	Linearity	Nernstian slope	reactant mixture with ISAB
NiS1-ISE	10^{-1} to 10^{-4}	y = -16.4x + 282.0 R² = 0.993	$Ni(NO_3)_2$
	10^{-1} to 10^{-5}	y = -16x + 298 R² = 0.996	$Ni(NO_3)_2$+Methanol
	10^{-1} to 10^{-6}	y = -16.34x + 294.5 R² = 0.995	$Ni(NO_3)_2$+Methanol+Ascorbic Acid
NiA1-ISE	10^{-1} to 10^{-4}	y = -18.59x + 291.0 R² = 0.999	$Ni(NO_3)_2$
	10^{-1} to 10^{-6}	y=-18.06x + 310.5 R² = 1	$Ni(NO_3)_2$+Methanol
	10^{-1} to 10^{-6}	y=-18.34x + 299.2 R² = 0.999	$Ni(NO_3)_2$+Methanol+Ascorbic Acid

Potentiometric Titration

End point determination in the titration of Ni^{2+} ion by standard EDTA solution using NiISE as indicator electrode is shown in Fig. 5. A sharp end point could be seen, though potential change not as large as expected for ISE. It is to be mentioned that absolute potential is not required in potentiometric titration. The results show that alkaline co-precipitation method results in good performing indicator electrode. The end point in both cases lies close to theoretical volume of 10mL of EDTA.
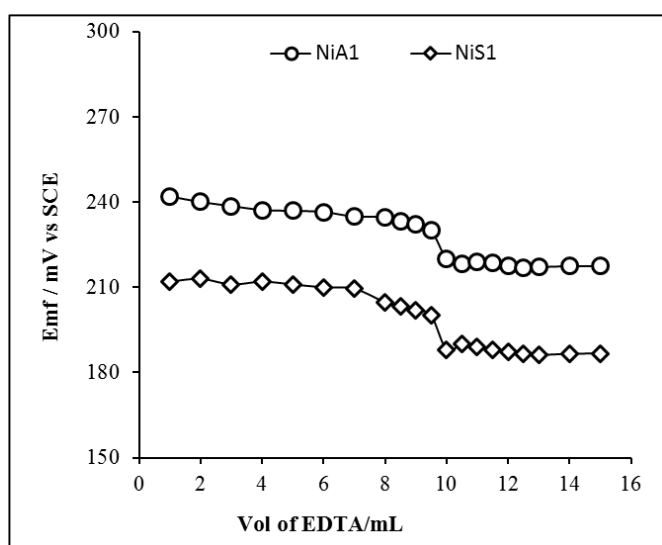

Fig 5: *Potentiometric titration of 10 mL Ni(NO₃)₂ solution using standard EDTA solution*

Effect of interfering ions

In this work, selectivity coefficients of the prepared electrodes towards different cationic species were evaluated by using match potential method. The effect of different interfering ions like $Pb(NO_3)_2$, Cd (NO3)$_2$, $NH_4(NO_3)$, Zn (NO3)$_2$, $NH_4(NO_3)$, and $Ag(NO_3)$ were tested. Both electrodes show similar interference behaviours. It was found that $PbSO_4$, $Cd(NO_3)_2$, $NH_4(NO_3)$, and Zn (NO3)$_2$, are more interfering towards the nickel than $Cu(NO_3)_2$, and $AgNO_3$. . The sequence of interference ions from higher to lower are found as follows order:

$Cd^{2+} > Pb^{2+} > NH_4^+ > Zn^{2+} > Ag^+ > Cu^{2+}$
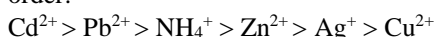
Conclusion

Co-precipitation of metal sulfides in alkaline medium resulted in well behaved Ni-ISE with better linearity (10^{-1} M to 10^{-1} M), low detection limit (10^{-6}M), better Nernstian slope (18mV/decade) and better surface morphology. Therefore, alkaline method which was introduced as new method for the preparation of active materials for sensor was found to result in better response and stability of the sensor.

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