Journal Homepage: -www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI:10.21474/IJAR01/12243
DOI URL: http://dx.doi.org/10.21474/IJAR01/12243

RESEARCH ARTICLE

PREPARATION AND STUDY OF ACETATE ION SENSITIVE ELECTRODE

Basant Lal[1] and Priya Sharma[2]

1. Department of Chemistry, Institute of Applied Science and Humanities, GLA University, Mathura,U. P., India - 281 406.Email: basant.lal@gla.ac.in
2. Department of Chemistry, B.S.A. College, Mathura,U. P., India - 281 004.

Manuscript Info

Manuscript History
Received: 31 October 2020
Final Accepted: 30 November 2020
Published: December 2020

Key words: -
Acetate Sensitive Electrode, Potentiometric Titration, PVC Method, Silicon Grease Method, Coated Wire Method And Pellet Method

Abstract

Various methods such as silicon grease, pellet, PVC and coated wire were employed for preparation of acetate sensitive electrode. Reproducibility of electrode potential, response time and their stability were investigated. The potential of electrode has been studied with different concentrations of acetate ion. These electrodes were used for direct potentiometric determination of acetate ion in food preservatives (vinegar sample), water and water-alcohol mixture solvents. Suitable empirical equations have been developed for reliability of data. Electrodes were also used as an end point detector in potentiometric titration.

Introduction:-

A number of metal-metal salts electrodes [1-5] have been prepared and studied to determine the concentration of anion of the respective metal salt used in the preparation of electrode. However, investigation of electrodes which can be respond to organic anions as well as sulphur containing organic anions are rather limited. This suggests that work may also be directed in this direction. Present investigation is mainly based on the development of acetate, dithioacetate, thiocarbamide and diethyl dithiocarbamide ions sensitive electrode by PVC method, silicon grease method, coated wire method and pellet method. Electrode characteristics like reproducibility, response time and stability/durability of electrodes have been evaluated and discussed to select the best working method of the electrode.

Sulphide [1-5], fluoride [6], bromide [7-8], iodide [9-13] acetate [14-16] and oxalate [17] anion sensitive electrode has beenprepared by a number of investigators using respective mercurous salts. Chloride anions [18-21] sensitive electrode based on silver chloride have been developed by a number of investigators which is very reproducible and fairly easy to prepare. This electrode has been used to investigate the thermodynamics of electrolytes in aqueous, partially aqueous and non aqueous solutions over a wide range of temperatures as well as in determining the dissociation constants of weak acids and bases accurately [22-26]. Sulphate ion sensitive electrode based on mercurous sulphate has been prepared and used to determine transport numbers and activity coefficients. The reproduce ability of this electrode has been shown to be ± 0.3 mV by measurement on sulphuric acid in the hydrous methanol [27-29] sulphate anion sensitive electrodes have been studied in details [30-34] as these electrodes found use in the lead accumulator. It is interesting to mention that under condition of slow discharge [35-36]. The cell reaction is strictly

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$

Corresponding Author:- Basant Lal
Address:- Department of Chemistry, Institute of Applied Science and Humanities, GLA University, Mathura,U. P., India – 281 406.

Proposed as early as 1882 by Gledstone and Tribe [37].Gurtu and coworker [38] have prepared a number of sulphide, thio-organic anions and other complex organic anions using simple methods and have been used them for direct potentiometric determinations of respective ions. Kushwaha and coworkers [39] have studied a number of anion sensitive membrane electrodes with respect to various electrode characteristics.

Ion-selective electrodes (ISEs) are small size, portable and economical [40] used in potentiometric measurements [41, 42] and also applicable in environmental [43], clinical [44] and food [45] analysis.

Materials and Methods: -

The equipment used for measurement of e.m.f.involvedifferent important parts of the apparatus such as potentiometric system, thermostat and standard half cell.

Potentiometric System: the e.m.f measurement was carried out by a portable potentiometer made by Toshniwal PL 52, which has built in standard cell and a robust taut suspension galvanometer was used and detections were measured with Bajaj make lamp and scale arrangement.

Thermostat: temperature of solution was maintained by mean of thermostatic water bath fitted with a toluene regulator.

Standard half cell: a saturated calomel electrode was used as a standard half cell. This cell has a low resistance and therefore, ensures good deflection in the galvanometer. The cell was occasionally checked against M/20 potassium hydrogen phthalate solution in order to ensure accuracy. For the purpose to prepare cell, dry and purified mercury was taken into a tapered tube (length 8 cm; diameter 1.5 cm) to a height of about 3 cm. A homogeneous paste consisting of 5 gm of mercury and 10 gm of calomel was prepared by rubbing together with a pestle in mortar made of glass and washed several times in a saturated solution of potassium chloride by the process of decantation. The paste was then poured over the surface of mercury in the tapered tube to a thickness of about 1 cm along with some crystals of potassium chloride. The tube was finally filled with a saturated solution of potassium chloride.

The mouth of tube was then closed with sulphur free rubber cork having a hole through which was passed a tube at the lower end of which a platinum wire was fused. The tube was so placed that the platinum wire should be dipped in the lowest mercury layer so that platinum wire could make electrical connection with the outer circuit through mercury placed inside the tube. A U-tube (length 4 cm) with one end of capillary size filled with a jelly consisting of one part of agar-agar and nine-part potassium chloride was joined to the tapered tube in such way that it was connected with the saturated potassium chloride solution in the tapered tube while the capillary end kept out.

The cell after its preparation was left for 24 hours to attain equilibrium. The capillary end was maintained in the conductivity water to prevent drying up of the agar-agar jelly.

Acetate Sensitive Electrode:

PCV Method:

A silver wire of length 2 cm and diameter 0.2 mm was fused in pyrex tubing of internal bore of about 5 mm in such way that about 1 cm length of it remained outside. It was cleaned with chromic acid and conductivity water and then immersed in a solution prepared by dissolving 90% silver acetate precipitate and 10% PVC in minimum possible volume of tetra hydrofurane. The solvent was evaporated using a water bath and the electrode was left to dry overnight. From the outer side of the tube a few cc of mercury was added and a copper wire was inserted for electrical connections. It was then kept immersed in 0.001M sodium acetate solution for 30 minutes for conditioning. The electrode was washed and then immersed in conductivity water for 24 hours. The electrode was now ready for use. To ensure the reproducibility over a long period of time, the electrode is maintained in conductivity water after use shown in figure1a.

Silicone Grease Method:

The freshly precipitated silver acetate was mixed with minimum quantity of non-reacting silicone grease (BDH England) thoroughly, using a glass spatula and a glass plate. This cohesive mixture was then sucked into a glass tube of internal bore 2 mm. From the other side a few cc of silver amalgam and mercury was added then a copper wire was inserted for electrical connections. It is then immersed in 0.001 M sodium acetate solution for 30 minutes for conditioning. The electrode was washed and kept immersed in conductivity water for 24 hours to attain equilibrium

potential. The electrode is now ready for use. To ensure the reproducibility over a long period of time, the electrode was maintained in conductivity water after use shown in figure 1b.

Coated Wire Method:
A platinum wire (length 2 cm, diameter 0.25 mm) was fused in a pyrex tube so that 1 cm of wire remained outside. The assembly was then cleaned with chromic acid mixture and finally with conductivity water. The assembly was then dried in electrical oven.

Silver was deposited electrically on the platinum wire using soluble silver cyanide complex, $KAg(CN)_2$, in excess of potassium cyanide. The current and voltage were so regulated that about 0.2 gm of silver was deposited in about half an hour. The silver electrode so prepared was washed in conductivity water and then kept immersed in pure aqueous acetic acid (1%) for sufficient time so as to get uniform coating of silver acetate on it.

Form the other side of the tube a few cc of mercury was added and a copper wire was inserted for electrical connections. The electrode was again washed in conductivity water and kept immersed in 0.001 M sodium acetate solution for 30 minutes for conditioning. The electrode was washed and kept immersed in conductivity water for 24 hours to attain equilibrium potential. To ensure reproducibility over a long period of time the electrode was maintained in conductivity water the electrode is shown in figure 1c.

Pellet Method:
The freshly precipitated silver acetate is pressed in a dye of tube used to press pellet for infrared analysis (Backmann instrument). The pellet is pressed at about 10^5 psi at room temperature under vacuum for about 2 hours. The pellet is made to stick to one of the end of tube using araldite. From the other side a few cc of silver amalgam and mercury are added and a copper wire is also inserted for making electrical connections. The whole assembly is conditioned in 0.001 M sodium acetate solution for 30 minutes and finally in conductivity water for 24 hours. The electrode was now ready for use. To ensure reproducibility over a long period of time, the electrode is maintained in conductivity water after use. The electrode is shown in figure 1d.

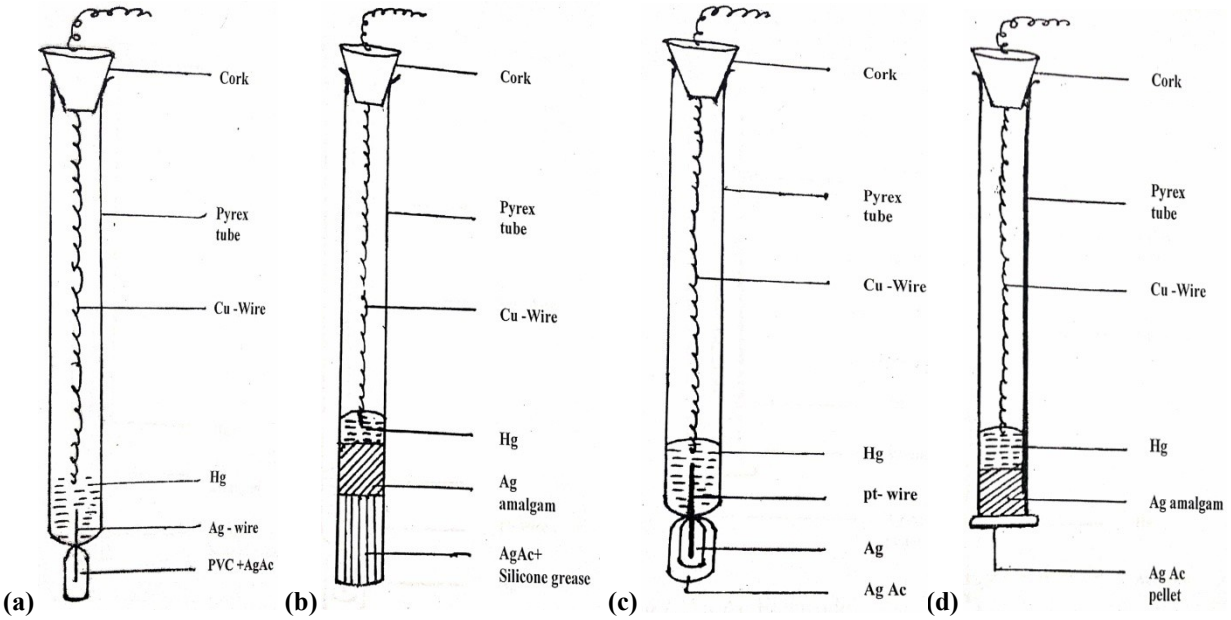

Fig. 1:- Acetate ion sensitive electrode prepared by different methods: **(a)** PVC method, **(b)** Silicon grease method, **(c)** Coated wire method and **(d)** Pellet method.

Result and Discussion:-

Reproducibility:
In orderto investigate the reproducibility of electrodes obtained by different methods, the electrode potential was recorded at two different concentrations of acetate ion and given in table 1.

Table 1:- Study of reproducibility behavior of the electrode potential of acetate ion sensitive electrodes at different concentrations of acetate ion in aqueous medium at 25^0C.

Electrode No.	Electrode potential (Volts)					
	Different concentrations of acetate ion in aqueous medium					
	2.51×10^{-3} M			2.51×10^{-2} M		
	PVC method	Silicon grease method	Coated wire method	PVC method	Silicon grease method	Coated wire method
1	0.164	0.165	0.164	0.224	0.222	0.220
2	0.160	0.164	0.160	0.219	0.223	0.216
3	0.167	0.167	0.166	0.227	0.225	0.225
4	0.173	0.162	0.158	0.235	0.219	0.208
5	0.169	0.161	0.161	0.228	0.220	0.212
6	0.164	0.165	0.168	0.223	0.221	0.231
7	0.158	0.170	0.162	0.214	0.228	0.225
8	0.153	0.162	0.171	0.209	0.218	0.235
9	0.164	0.169	0.153	0.224	0.227	0.212
10	0.166	0.166	0.162	0.229	0.221	0.215

As evident from the table 1, all the ten electrodes gave similar values of electrodes potentials at different acetate ion concentration. Standard deviation of the electrode potential prepared by PCV, silicon grease and coated wire methods are worked out to be ±6.6 mV, ±3.1 mV and ±8.2 mV, respectively. A representative graph of electrode potential of ten different electrodes prepared by silicon grease method at 2×10^{-3} M and 2×10^{-2} M of acetate ion concentrations shows reproducible behavior with very less standard deviation (Fig. 2).

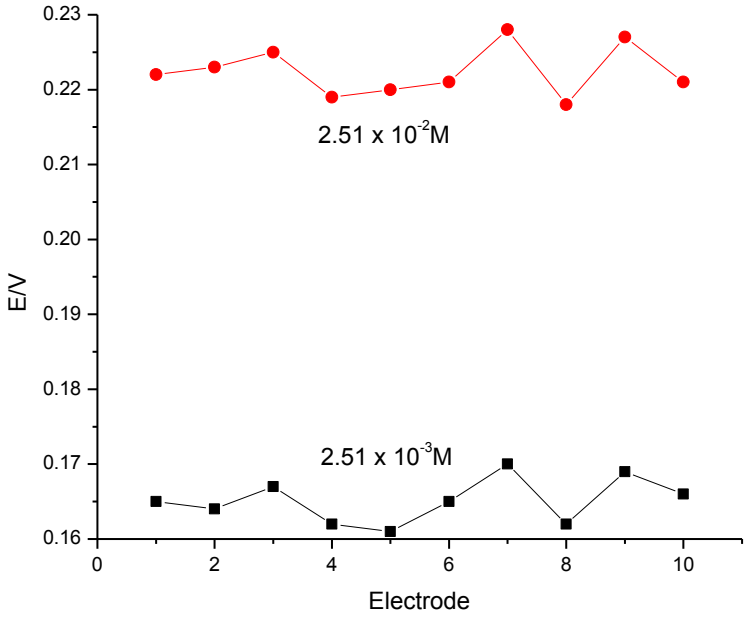

Fig. 2 Reproducible behaviour of different electrodes prepared by silicon grease method.

Response Time and Stability:

Stability test of electrode prepared by different methods were performed by measuring the electrode potential of each electrode at different concentration of acetate ion in aqueous medium towards time required to established equilibrium potential at 25^0C and the results so obtained are shown in table 2.

Table 2:- Study of response behavior of the electrode potential of acetate ion sensitive electrodes prepared by different method at different concentrations of acetate ion in aqueous medium towards time required to reach equilibrium potential at 25^0C.

Time in	Electrode potential (Volts)

minutes	Different concentrations of acetate ion in aqueous medium					
	2.51×10^{-3} M			2.51×10^{-2} M		
	PVC method	Silicon grease method	Coated wire method	PVC method	Silicon grease method	Coated wire method
0.5	0.079	0.082	0.089	0.149	0.141	0.133
1.0	0.112	0.115	0.105	0.172	0.169	0.151
2.0	0.149	0.165	0.128	0.201	0.222	0.175
3.0	0.164	0.165	0.140	0.223	0.222	0.189
4.0	0.164	0.165	0.151	0.224	0.222	0.202
5.0	0.164	0.165	0.164	0.224	0.222	0.220
10.0	0.164	0.165	0.164	0.224	0.222	0.220
20.0	0.164	0.165	0.164	0.224	0.222	0.220
30.0	0.164	0.165	0.164	0.224	0.222	0.220
40.0	0.164	0.165	0.164	0.224	0.222	0.220

From the above table it is seen that the values of electrode potential become constant within 3, 2 and 5 minutes for PVC, silicon grease and coated wire method, respectively and remain steady up to 40 minutes. After use the electrode must be kept immersed in conductivity water for conditioning of the electrode. The electrode potential values were plotted against response time and shown in Figure 3(a, b and c).

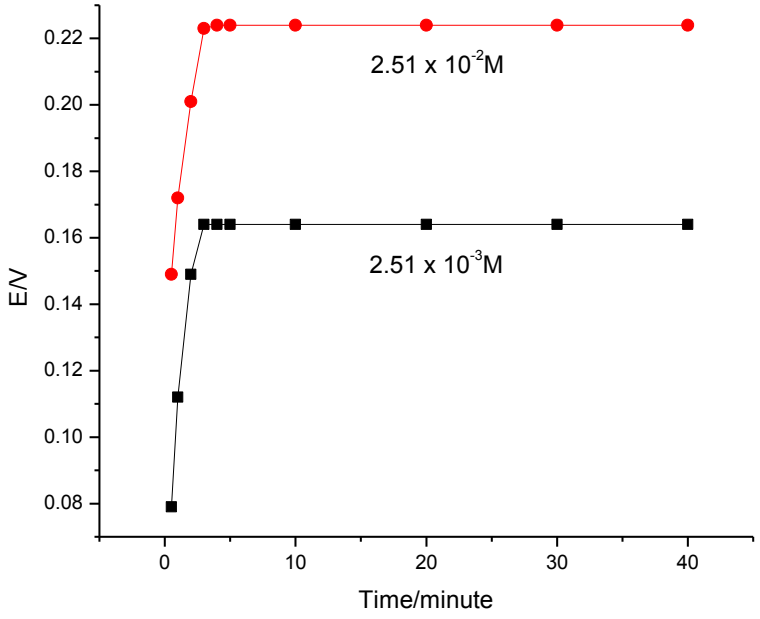

Fig. 3a Potential of electrode prepared by PVC method vs responce time

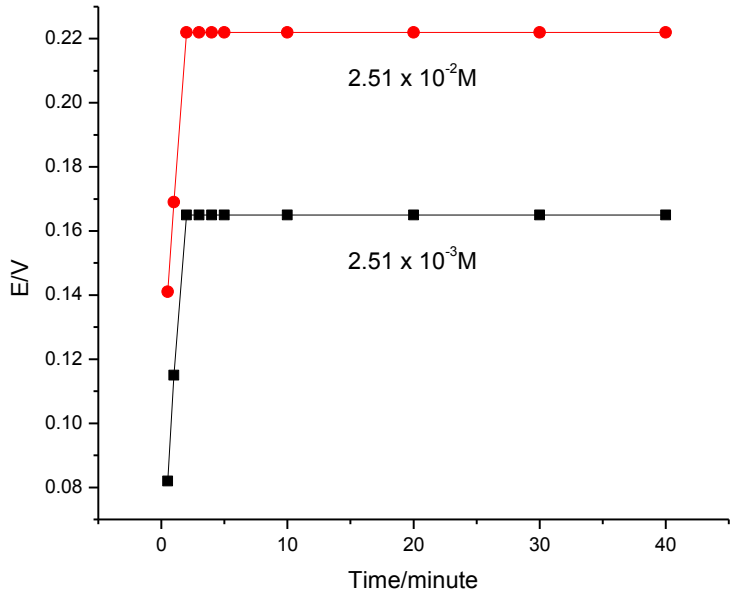

Fig. 3b Electrode potential prepared by silicon grease method vs response time

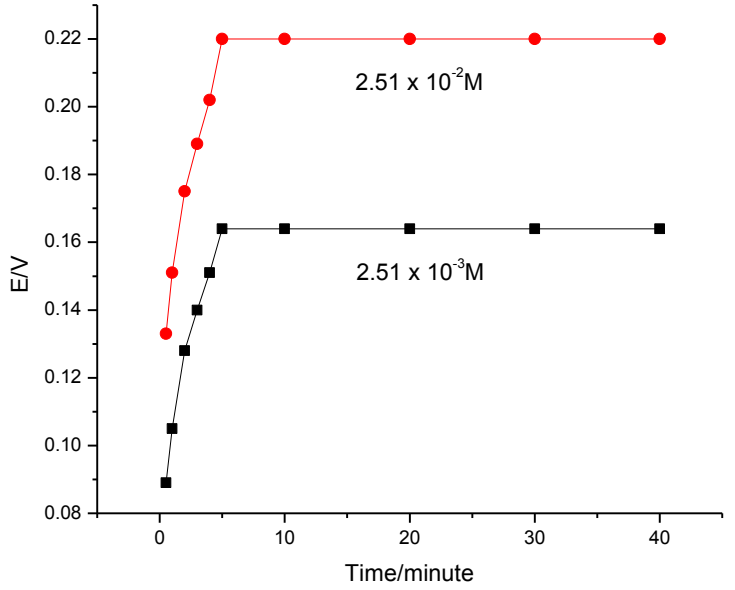

Fig. 3c Potential of electrode prepared by coated wire method vs response time

Table 3:- Study of stability behavior of the electrode potential of acetate ion sensitive electrodes prepared by different methods with different concentrations of acetate ion in aqueous medium over a long period of time at 25^0C.

Time in months	**Electrode potential (Volts)**					
	Different concentrations of acetate ion in aqueous medium					
	2.51 x 10^{-3} M			**2.51 x 10^{-2} M**		
	PVC method	**Silicon grease method**	**Coated wire method**	**PVC method**	**Silicon grease method**	**Coated wire method**
0	0.164	0.165	0.164	0.224	0.222	0.220

5	0.167	0.164	0.165	0.228	0.221	0.221
10	0.162	0.165	0.163	0.222	0.224	0.220
15	0.165	-	0.164	0.227	-	0.218
20	-	-	-	-	-	-

The electrode is stable up to 15, 10, 15 months for the acetate ion sensitive electrode prepared by PVC method, silicon grease method and coated wire method, respectively. If maintained in conductivity water and kept away from dust particles. The variation in the values of electrode potential is within the range of standard deviation worked out for these electrodes and shown in figure 4.

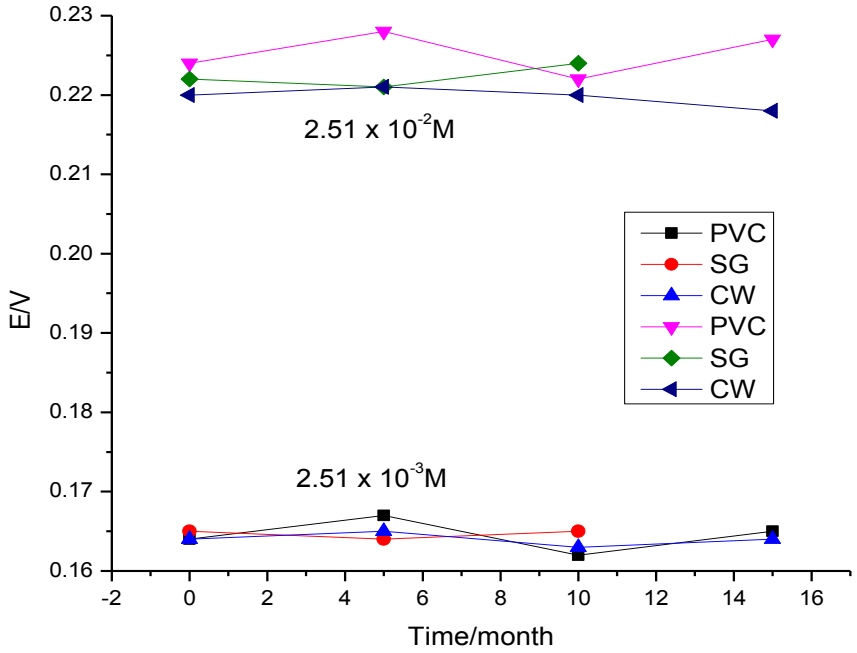

Fig.4 Stability behaviour of acetate senstive electrode at two different concentrations

Conclusions:-

Following conclusions are withdrawn from these investigations:

1. Acetate ion sensitive electrode has been found suitable as an indicator electrode for acetate ion.
2. The acetate ion sensitive electrode has been prepared by four different methods viz., PVC method, silicon grease method, coated wire method and pellet method.
3. The pellet method did not perform well and so the electrode prepared by this method was not studied further.
4. The standard deviation values of the potential of the acetate sensitive electrodes prepared by the three methods, viz., PVC method, silicon grease method and coated wire method are in the following order:Silicon grease type (±3.1) < PVC type (±6.6) < coated wire type (±8.2
5. The response time values of the acetate sensitive electrodes prepared by three methods, viz., PVC method, silicon grease method and coated wire method are in the following order: Silicon grease type (2) < PVC type (3) < coated wire type (5)
6. The stability of acetate sensitive electrode prepared by three methods viz., PVC method, silicon grease method and coated wire method are in the following order: Silicon grease type (10) < PVC type (15) = coated wire type (15
7. The acetate sensitive electrode was maintained in conductivity water away from the dust particles after used so that their response towards acetate solutions may remained unaltered.
8. It is recommended that further study should be done with the electrode prepared by silicon grease method as this electrode was found to be more accurate with less response time.
9. It is further recommended that acetate sensitive electrode may be used as an end point detector for potentiometric titration for acetate solution with metals.

Acknowledgments:-
The authors express their sincere thanks to Dr. L.R. Singh (former HOD) and Prof. Ashok Kumar, Department of Chemistry, BSA College Mathura for their valuable help and support to complete this investigation.

Reference:-
1. Scarliarini, G. and Pratesi, P., Atti Accad. Liucei, 11, 193 (1930).
2. Kremer, V. A., and Vail, E.L., V.S.S.R., 109 Feb. 25, 853 (1958).
3. Golding R. M., J. Chem. Soc., 1838 (1959).
4. Shepeizer, G.M. and Zaidman, N.M., Zavodsk. Lab., 31, 272 (1965).
5. Cadersky, I. and Pribyl, M., Z. Anal. Chem., 217, 252 (1966).
6. Koeber, G.G. and D.E. Vries, T., J. Am. Chem. Soc., 74, 5008 (1952).
7. Goodwin H.M., Z. Physik Chem., 13, 577 (1894).
8. Bugarsky, S., Z. Anorg. Chem., 14, 145 (1897).
9. Gupta S.R., Ph.D. Thesis, London, 1957.
10. Vosburgh, W.C., J. Am. Chem. Soc., 49, 2222 (1927).
11. Gerke, R.H., Chem. Revs. I, 385 (1925).
12. Bates, R.G. and Vosburgh, W.C., J. Am. Chem. Soc., 59, 1188 (1957).
13. Owen B.B., J. Am. Chem. Soc., 57, 1626 (1925).
14. Burgarsky, S., Z. Anorg Chem., 14, 145 (1957).
15. Larson W.D. and Macdougall F.H., J Phys. Chem., 41, 493 (1937).
16. Larson W.D. and Tomosiecek, W.J., J. Am. Chem. Soc., 61, 65 (1941).
17. Larson W.D. and Tomosiecek, W.J., J. Am. Chem. Soc., 63, 3329 (1941).
18. Owen B.B., J. Am. Chem. Soc., 60, 2229 (1938).
19. Hills, G.L. and Ives, D.J.G., J. Chem. Soc., 1951, 305.
20. Gledhill, J.A. and Mohan, G. McP., Trans Faraday Soc., 1951, 305.
21. Guggenheim, E.A., and Prue, J.E. Trans Faraday Soc., 50, 231 (1952).
22. Harned, H.S. and Owen, B.B., "Phy. Chem. Electro, Solutions" 3rd Ed. Reinhold, New York, 1958.
23. Maclnnes, D.A., "Principle of Electrochemistry" Reinhold, New York 1939.
24. Janz, G.J. and Gordon, A.R., J. Am. Chem. Soc., 65, 218 (1943).
25. Nonhebel, G. and Hartley, G.S., Phil. Mag., No6, 729 (1925).
26. Woolcock, J.W. and Hartley H., Phil. Mag., No7, 1133 (1928).
27. Hulett, G.A., Phys. Reev., 32, 257 (1911).
28. Ferguson, A.L. and France W.G., J. Am. Chem. Soc., 43, 2150 (1921).
29. Kanning, E.W. and Bowman, M.G., J. Am. Chem. Soc., 68, 2043 (1946).
30. Bray, U.B., J. Am. Chem. Soc., 49, 2372 (1927).
31. Cowperth Waite, I.A. and Lamer V.K., J. Am. Chem. Soc., 53, 4333 (1931).
32. Beck, W.H., Singh K.P. and Wynne-Jones, Trans. Faraday Soc., 55, 331 (1959).
33. Hamer W.J., J. Am. Chem. Soc., 57, 9 (1935).
34. Harned H.S. and Hamer, W.J., J. Am. Chem. Soc., 57, 27 (1935).
35. Beck W.H., Lind, R. and Wynne-Jones, Trans. Faraday Soc., 50, 136 (1954).
36. Beck W.H., Lind, R. and Wynne-Jones, Trans. Faraday Soc., 50, 147 (1954).
37. Godstone, J.H. and Tribe, A., Nature 25, 221, 461 (1881)., 26,251, 342, 603 (1881)., 27, 583 (1883).
38. Gurtu and Coworkers, Convention of chemistat IIT Powai, 1980., J. Electrochem. Soc., India, 201 (1987)., Ind. Sci. Cong., Madurai (1989)., Ind. Sci. Cong., Cochin (1990)., Ind. Sci. Cong., Indore (1991).
39. Kushwaha et al., Ind. J. Chem., 31 A, 439 (1992)., U. Scientist., Phyl. Sciences, 1, 19 (1996)., Ind. J. Chem., 40 A, 270 (2001)., J. Chem. Enviro. Res., 12 (2003)., J. Ind. Council Chemists, 22, 23 (2005).
40. Bakker E., Bu¨hlmann P., and Pretsch E., Chem. Rev. 1997, 97, 3083–3132.
41. Bu¨hlmann P. and Chen L. D., in Supramol. Chem., John Wiley & Sons, Ltd, 2012.
42. Mikhelson K. N., Ion-Selective Electrodes, Springer, 2013.
43. De Marco R., Clarke G.and Pejcic B., Electroanalysis 2007, 19, 1987–2001.
44. Oesch U., Ammann D.and Simon W., Clin. Chem. 1986, 32, 1448–1459.
45. Deisingh A. K., Stone D. C. and Thompson M., Int. J. Food Sci. Technol. 2004, 39, 587–604.
46. Martin K., Kadam S. A., Mattinen U., Bobacka J.and Leito I., Electroanalysis 2019,31, 1-7.