THE 4th ANNUAL INTERNATIONAL SEMINAR ON TRENDS IN SCIENCE AND SCIENCE EDUCATION 2017 State University of Medan November 14th - 15th Grand Mercure Hotel. Jl. Sutomo. No. 1. Medan. Indonesia

The Characteristics Membrane PVA-Enzyme and Coating PVC-Plasticizer with XRD

Abd Hakim S[1],Krista Tarigan[2], Krista Sebayang[2], Manihar Situmorang[1], Timbangen Sembiring[2]

[1]Physics Departement , Universitas Negeri Medan,Medan, Indonesia
[2]Program Magister Ilmu Fisika, Universitas Sumatera Utara, Medan, Indonesia

ABSTRACT

This study was aimed to characterize PVA-coating membrane PVC-plastisisier membrane through XRD absorption spectrum, density and elemental completeness using Match program. The method used membrane immobilization at the indicator electrode. Selection stage of indicator electrode by dipping tungsten electrode with PVA 0.0350 g - enzyme 6 mg, then in coating with PVC 0.0350 g - plasticizer 0.0500 g. The results obtained electrode indicator of tungsten immobilized metal PVA 0.0350 g and enzyme 6 mg dyeing 2 times coating THF solution 10 mL, PVC 0.0350 g and plasticizer 0.0500 g 1 times from absorption spectrum and Match program.

Keywords: Spectrum absorption, immobilization membrane, PVA enzyme, PVC-plastisier coating.

Corresponding Author: Abd Hakim S, 1Physics Departement, Universitas Negeri Medan, Medan, Indonesia.Email: abdhakims07@gmail.com

INTRODUCTION

Determination of urea performed using potentiometric biosensor in ion-selective electrida (ISE) (Jaworska et al, 2015). The analyte binds the bioreceptor on the surface of the indicator electrode in the buffer solution, resulting in a potential difference-change between the two electrodes, this change measured by the system. Selected electrode reference electrode Ag / AgCl and selected indicator electrode ISE (Barbosa, AR, 2011) with a metal electrode of tungsten (Schonauer, D., 2013).

The analyses of the research are urea analysts, the detection element is the problem of research needs modification related to potentiometric ion (ISE) ionometric biosensor method. The modification on the electrode membrane is the immobilized membrane with PVA coting substrate with PVC plaster matrix with plastisiser additive. Metal immobilization mechanism includes the process of ion exchange, surface *complexation,* mineral *dissolution* (Mignardi et al, 2013). The membrane is a thin film because the electrodes immobilized by the enzyme through immersion in the enzyme PVA solution are then coated. Characterization of thin films based biosensor developed with thin film technology which has prospects in the field of biotechnology and bio-electronics (Dey & Goswami, 2013), biotechnology and bio-electronics developed from bio-molecular electronics.

The recombination of proteins into a network using Poly (Vinyl Alcohol) PVA is chemically followed by spectroscopic characterization. PVA is an alternative for the detection of material, is soluble in water, very versatile for a modified improve the mechanical and chemical properties (Mansur et al, 2008).

PVC membrane electrode, receptors (ionophore) with the low solubility of the film polymer in conventional organic and non-organic solvent (Broncová et al, 2008). Enzyme immobilization method according to the physical properties (adhesion, Inclusi) and chemical properties *(cross-linking),* PVC as urease medium on the surface of the glass electrode for mounting directly on the membrane enzyme (Jaworska et al, 2015). Adhesion is used for the isolation of the transducer and the electric part of the coating on the ion-selective membrane.

PVA and PVC is a polymer, the polymer can act as an electrode material in the redox activity connected to specific potential (Apetrei et al, 2015), through oxidation (p-doping) and reduction (n-doping) reaches for conduction *carrier.* Electrochemical synthesis requires a monomer base in the solvent according to an anodic potential on the indicator electrode that pushes toward the oxidation of the monomer. Polymer type described three forms of electrodes (Apetrei et al, 2015) (working, *counter,* and reference electrode) in a solution of monomers, solvents and electrolytes according to the doping rules.

Based on the above researchers chose the title "Character PVA-Enzyme Membrane Coating PVC-Plastisisier by XRD".

MATERIAL AND METHODS

Chemicals and material: The material used in the study is a standard urea 56 180 Sigma-Aldrich, the enzyme EC 3.5.1.5 (Urease) U4002, 50-100 ku types ix, PVA [-CH 2 CHOH-] n, PVC (CH 2 CHCl) n, potassium tetrakis 4-chlorophenyl borate (CLC 6 H 4) 4 BK, Tetrahydrofuran C 4 H 8 O, were from Sigma-Aldrich and the method used is the potentiometric method.

Tools (Tools): The equipment used is from Physics Laboratory and Chemical Laboratory of Medan State University in accordance with its use as follows is XRD-6100 Shimadzu.

Procedure of membrane and membrane electrode making with XRD: Coating I consists of a solution of 10 ml of THF is mixed PVC KTpClPB 0.5040 g and 0.0120 g. Coating II consists of a solution of 10 ml of THF is mixed with PVC 0. KTpClPB 0350 g and 0.0500 g.Membranes and membrane electrode at a table with a wavelength diffraction analysis 1.540600 ^{o}A, step size 0.020 with a range of data: (1) PVA membrane 0.5040 g + Enzymes are 7000 o A - 70000 o A (b) PVA 0.0350 g + Enzymes is 7050 ^{o} A - 70050 ^{o} A (c) PVA 0.5040 g Enzyme-Coating I is 7010 o A - 70010 ^{o} A, (d) PVA 0.0350 g Enzyme-Coating I is 7070 ^{o} A - 70 070 ^{o} A, (e) PVA 0.0350 g enzyme-Coating II is 7000 ^{o} A - 70000 ^{o} A. (2) The electrode membrane (a) 1x is 10080 ^{o} A -

70080 ^{o} A, (b) 2x is 10000 ^{o} A - 70000 ^{o} A, (c) 3x is 9800 ^{o} A - 69600 ^{o} A, (d) 4x is 9900 ^{o} A - 69900 ^{o} A, and (e) 5x is 7000 ^{o} A - 70000 ^{o} A dyeing the PVA membrane enzyme Coating 0.5040 g + I. (3) Membrane electrode (a) 1x is 6930 ^{o} A - 163811 ^{o} A, (b) 2x is 7000 ^{o} A - 70000 ^{o} A, (c) 3x is 7020 ^{o} A 70020 ^{o} A, (d) 4x is 7020 ^{o} A - 70020 ^{o} A, and (e) 5x 7000 ^{o} A - 70000 ^{o} A dyeing the PVA membrane enzyme 0.0350 g + Coating II.The absorption spectrum results from XRD were analyzed by Match program to determine the density of the water-soluble and water-insoluble material.

RESULTS AND DISCUSSIONS

Electrode membrane characterization with XRD: The spectrum of absorption membranes (a) PVA 0.5040 g + Enzymes are 7000 ^{o} A - 70000 ^{o} A (b) PVA 0.0350 g + Enzymes are 7050 ^{o} A - 70050 ^{o} A (c) PVA 0.5040 g Enzyme-Coating I is 7010 ^{o} A - 70010 ^{o} A, (d)PVA 0.0350 g enzyme-Coating I is 7070 ^{o} A - 70 070 ^{o} A, (e) PVA 0.0350 g enzyme-Coating II is 7000 ^{o} A - 70000 ^{o} A.

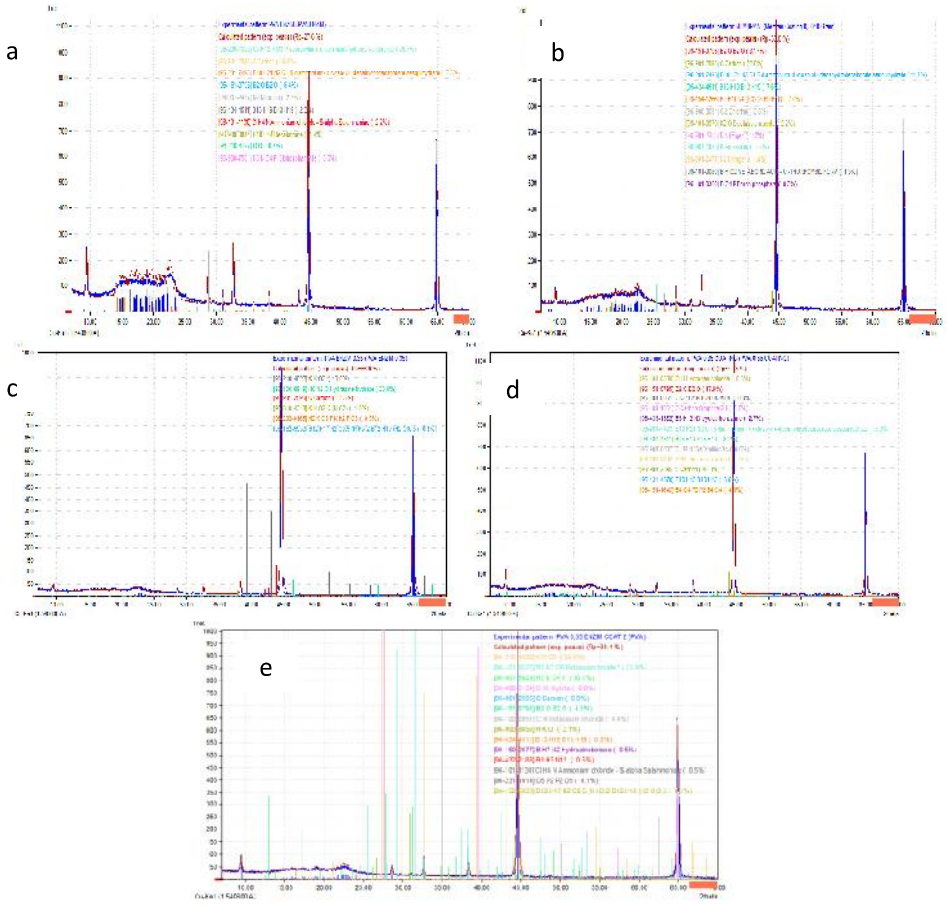


Figure 1. Membrane spectrum characterization (a) PVA 0.5040 g + Enzyme, (b) PVA 0.0350 g + Enzyme (c) PVA 0.5040 g Enzyme-Coating I, (d) PVA 0.0350 g Enzyme-Coating I, (e) PVA 0.0350 g Enzyme-Coating II with XRD, there is conformity with (Zhang et al, 2015).

Once analyzed by making a comparison of each absorption spectrum obtained as shown in FIG. 2.

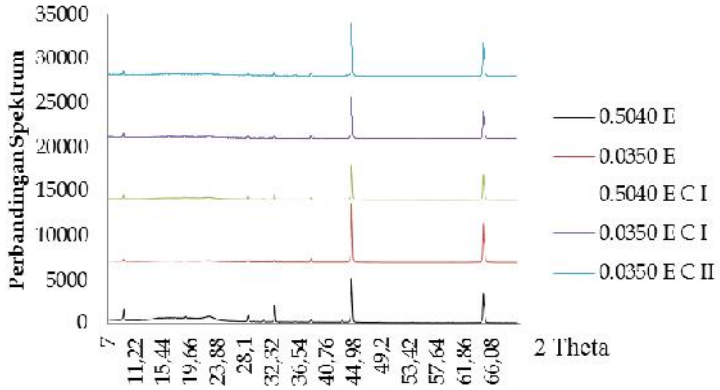


Figure 2. Comparison of membrane spectra (—) PVA 0.5040 g + Enzyme, (—) PVA 0.0350 g + Enzyme (—) PVA 0.5040 g Coating I, (—) PVA 0.0350 g Coating I (—) PVA 0.0350 g Enzyme-Coating II with XRD.

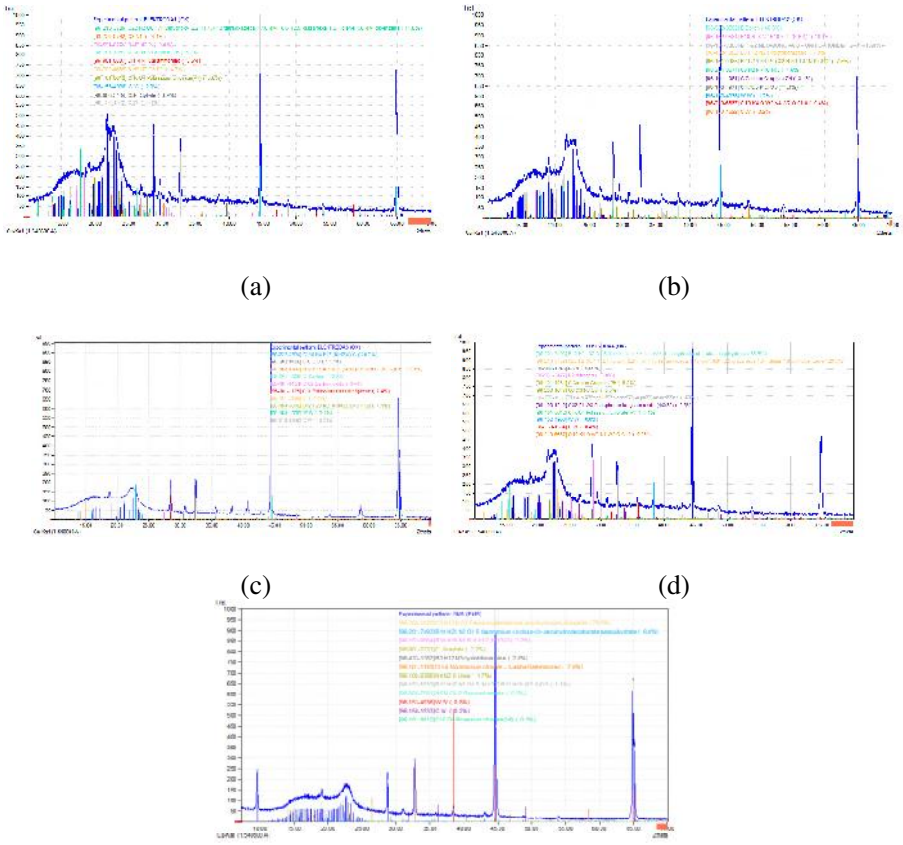
Table 1. PVA 0.0350 g Enzyme-Coating II with XRD

Amount (%)	Formula	Crystal system	Cell parameters	Calc. density
38.6	KNO3	trigonal (hexagonal axes)	a= 5.4698 Å c= 8.9920 Å	2.161 g/cm³
21.9	B3K3O6	rhombohedral	a= 7.7600 Å α= 110.600°	2.373 g/cm³
10.1	H2KO4P	tetragonal	a= 9.0610 Å c= 10.2840 Å	2.141 g/cm³
8.8	ClK	Cubic	a= 6.4220 Å	1.870 g/cm³
6.9	C	trigonal (hexagonal axes)	a= 2.5221 Å c= 43.2450 Å	3.516 g/cm³
4.5	B2O	trigonal (hexagonal axes)	a= 2.8790 Å c= 7.0520 Å	2.467 g/cm³
4.4	ClK	Cubic	a= 3.6340 Å	2.579 g/cm³
2.1	HKO	Cubic	a= 5.7800 Å	1.929 g/cm³
0.8	B13H19	monoclinic	a= 9.2170 Å b= 6.4980 Å c= 19.7190 Å β= 97.690 °	0.906 g/cm³
0.5	BH7N2	orthorhombic	a= 12.9740 Å b= 5.0702 Å c= 9.5069 Å	0.972 g/cm³
0.5	B3H3N12	triclinic (anorthic)	a= 8.5790 Å b= 9.1820 Å c= 12.0430 Å α= 104.620° β= 90.260 ° γ= 110.740 °	1.584 g/cm³
0.5	ClH4N	Cubic	a= 3.8680 Å	1.437 g/cm³
0.1	O5P2	trigonal (hexagonal axes)	a= 10.2000 Å c= 13.5000 Å	2.325 g/cm³
0.1	B12H17N2O0.5	Orthorhombic	a= 22.9900 Å b= 10.2930 Å c= 9.3230 Å	0.996 g/cm³
13.5	*Unidentified peak area*			

Type of diffraction at the top of membrane with wavelength 1.540600 A ( ) PVA 0.5040 g + Enzyme (2θ = 9.74, 23.94, 28.88, 32.72, 44.56, 64.86) highest peak at 44.56, ( ) PVA 0.0350 g +

Enzyme (2θ = 9.46, 22.56, 28.64, 31, 32.67, 44.56, 64.87 peak is highest at 44.56, ( ) PVA 0.5040 g Enzyme-Coating I (2θ = 9.51, 22.64, 28.69, 32.71, 38.39, 44.61, 64.91 peak is highest at 44.61, ( ) PVA 0.0350 g Enzyme-Coating I (2θ = 9.51, 22.64, 28.69, 32.71, 38.39, 44.61, 64.91) highest peak at 44.61, ( ) PVA 0.0350 g Enzyme-Coating II (2θ = 9.53, 22.64, 25.09, 28.71, 32.76, 44.62, 64.93) The highest peak at 44.62 PVA 0.0350 g Enzyme-Coating II, followed by the second highest peak

Based on the highest peak in PVA 0.0350 g Enzyme-Coating II using Match program can be seen in table 1 formula and density. The elements contained in the formula are W, Cl, C, O, K, P, B, H.



(a) (b) (c) (d) (e)

Figure 3. XRD spectrum analysis with Match program of electrode (a) 1x, b) 2x, (c) 3x, (d) 4x, and (e) 5x immersion with PVA membrane 0.5040 g + Coating I enzyme

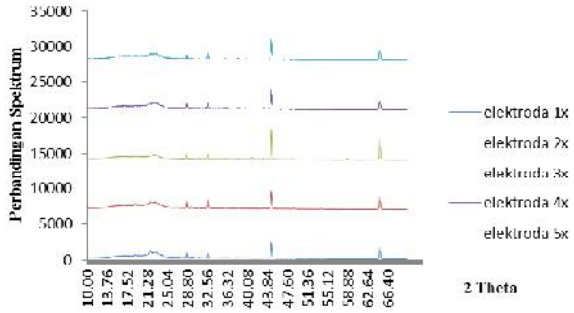
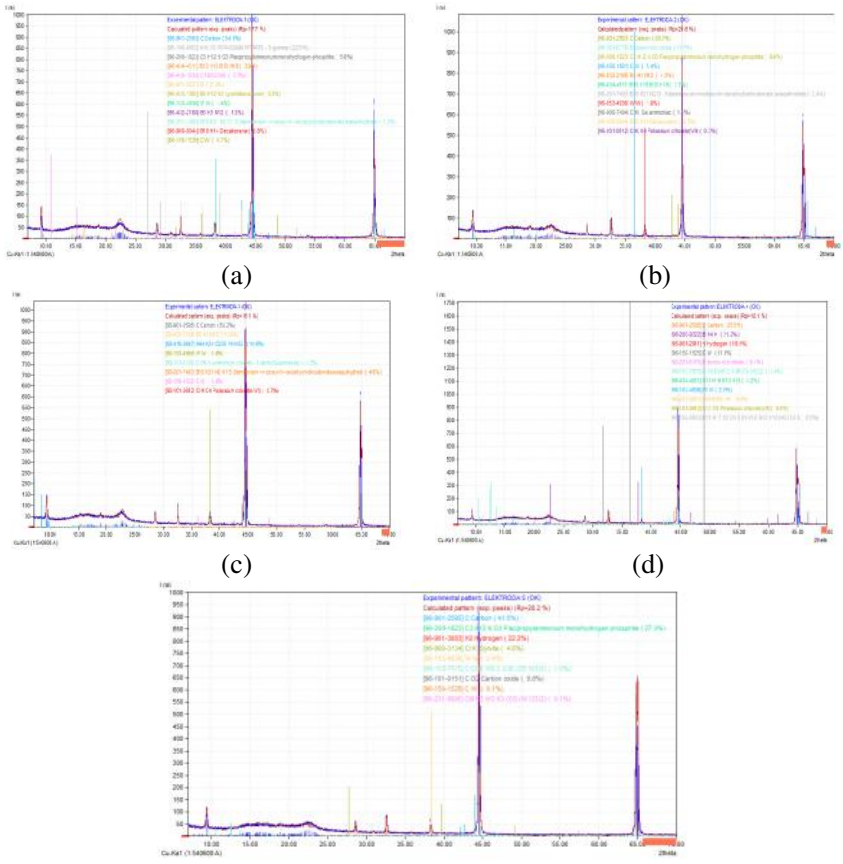


Figure 4. XRD spectrum of electrode (a) 1x, (b) 2x, (c) 3x, (d) 4x, and (e) 5x immersion with PVA membrane 0.5040 g + Coating I enzyme, best on 3x electrode.

Table 2. Membrane PVA 0.5040 g Enzyme Coating I to electrode 3x with XRD.

Formula	Amount (%)	Crystal system	Cell parameters	Calc. density
C3H12NO3P	84.6	orthorhombic	a= 8.1250 Å b= 12.6770 Å c= 7.1720 Å	1.268 g/cm³
ClH8N4P	4.1	orthorhombic	a= 4.7080 Å b= 16.2230 Å c= 7.5630 Å	1.500 g/cm³
CO	2.8	hexagonal	a= 3.6150 Å c= 5.8800 Å	1.397 g/cm³
B12H17N2O0.5	2.2	orthorhombic	a= 22.9900 Å b= 10.2930 Å c= 9.3230 Å	0.996 g/cm³
C	2.0	hexagonal	a= 4.8900 Å c= 3.8800 Å	2.482 g/cm³
CO2	1.5	cubic	a= 5.6300 Å	1.638 g/cm³
ClK	1.2	cubic	a= 6.2770 Å	2.002 g/cm³
C	0.6	hexagonal	a= 2.4686 Å c= 8.8408 Å	1.709 g/cm³
B12H20N2	0.5	cubic	a= 10.8781 Å	0.917 g/cm³
W	0.5	cubic	a= 4.0600 Å	18.245 g/cm³
CW	0.0	hexagonal	a= 2.9039 Å c= 2.8293 Å	15.740 g/cm³
Unidentified peak area	*25.4*			

PVA 0.5040 g coating enzyme was also done in Fig. 3, the analysis in Fig. 4. Match program can be seen in table 2 of formula and density. Similarly, PVA 0.0350 g of coating enzyme II was identified in Figure 5, the analysis in Figure 6. Match program can be seen in table 3 of formula and density.



(a) (b) (c) (d) (e)

Figure 5. XRD spectrum analysis with Match program of electrode (a) 1x, (b) 2x, (c) 3x, (d) 4x, and (e) 5x immersion with PVA membrane 0.0350 g + enzyme Coating II

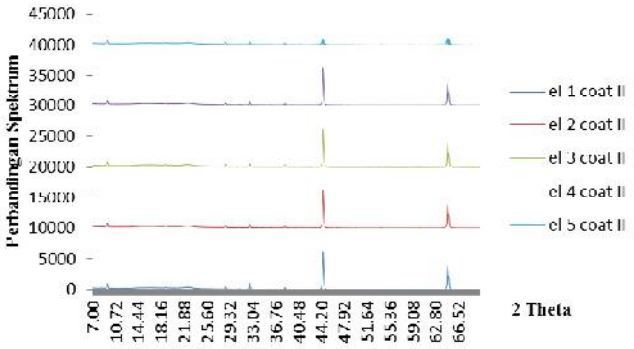


Figure 6. XRD spectrum of electrode (a) 1x, (b) 2x, (c) 3x, (d) 4x, and (e) 5x immersion with PVA membrane 0.0350 g + enzyme Coating II

XRD diffraction patterns (Mignardi et al., 2013) can be used to determine the best immobilization of the PVA electrode membrane of the PVC-plasticisation coating enzyme to the amount of electrode immersion. Effect of coating concentration solution on PVA-plastisisier PVA enzyme from membrane composite (WPVA: WPVC-plasticizers = 1: 1) (Niu et al, 2013) continuous change of permeability gradually decreases and separation factor increases with increasing concentration of coating solution. Composition of PVA 0.0350 g and PVC 0.0350 g plastisizer 0.0500 g ie 1: 1 shows the best results of the composition being experimented. When compared to the polymer composition with plasticizer 0.0350: 0.0500 is 70% plasticizer.

Table 3. Membrane PVA 0.0350 g Enzyme Coating II to elekcrode 2x with XRD.

Formula	Amount (%)	Crystal system	Cell parameters	Calc. density
C	60.2	hexagonal	a= 2.5221 Å c= 16.4743 Å	3.516 g/cm³
B	11.1	tetragonal	a= 8.7979 Å c= 5.0370 Å	2.209 g/cm³
C3H12NO3P	8.4	orthorhombic	a= 8.1250 Å b= 12.6770 Å c= 7.1720 Å	1.268 g/cm³
CW	5.4	hexagonal	a= 2.8446 Å c= 2.7939 Å	16.611 g/cm³
B3H3N12	4.3	triclinic (anorthic)	a= 8.5790 Å b= 9.1820 Å c= 12.0430 Å α= 104.620° β= 90.260 ° γ= 110.740 °	1.584 g/cm³
B13H19	3.7	monoclinic	a= 9.2170 Å b= 6.4980 Å c= 19.7190 Å β= 97.690 °	0.906 g/cm³
B10H21N2O1.5	2.4	monoclinic	a= 11.6740 Å b= 8.6230 Å c= 23.3180 Å β= 98.970 °	1.038 g/cm³
W	1.9	cubic	a= 4.0600 Å	18.245 g/cm³
ClN	1.5	cubic	a= 3.8771 Å	1.409 g/cm³
B10H14	0.7	monoclinic	a= 14.3700 Å b= 20.9800 Å c= 5.6900 Å γ= 90.000 °	0.834 g/cm³
ClKO4	0.3	orthorhombic	a= 8.8340 Å b= 5.6500 Å c= 7.2400 Å	2.546 g/cm³
Unidentified peak area	*24.0*			

The polymer matrix of a membrane varies considerably as follows: 33% polymer matrix, 66% plasticizer for matrix homogenization and 1% ionophore (Faridbod et al, 2008), 33 wt% polymer matrix, 66 wt% Potassium tetrakis (4-chlorophenyl) borate (K -TpClPB) membrane material and 1 wt% receptor (Krajewsk et al, 2007), (Othman and Houseini, 2011) membrane composition of 30: 68: 2 wt.%, The composition of the matrix of the electrode membrane in PVC is 1-7% ionophore, 28- 33% PVC (internal matrix), 60-69% plastisiser (solvent) and 0.03-2% cationic or anionic lipophilic salt as the adamant membrane (Mohammadi et al, 2010) the comparison affects the sensitivity and selectivity of ion selective electrodes. The natural properties of plastisiser increase the sensitivity and stability of the basic PVC sensor (Han et al, 2011) composition of ionophore 2.0% -5.0%: PVC 30.0%: plastisiser 65.0% - 68.0%, solid contact electrode contains three layers Pt / Electro-Conductive polymer / PVC film with ionophore.To improve the plasticizer composition of 0.0350 g of PVA is 0.0210 g (60%), 0.0231 g (66%), 0.0238 g (68%), 0.0242 g (69%).

The membrane used to separate the water of a characteristic having a mass of a type less than 1 g / cm 3 indicates the separating nature of the sample water such as oil with water, but when floating indicates a water-soluble substance such as water with salt, the sink indicates a water insoluble substance (solvent) 2.56 g / cm3. According to table 1 till 3 there is a component that has a small density of 1 g / cm3 as well as tables 1 till 3 except for table 4.21, table 4.21 is not the best electrode.

CONCLUSION

Conclusion: Based on the result and discussion of the research, the conclusion of the research is the need to repair the plasticizer composition of 0.0210 g (60%), 0.0231 g (66%), 0.0238 g (68%), 0.0242 g (69%) of 0.0350 g PVA. Suggestion: Suggestions for the manufacture of sensors from ISE-urea is based on observations and discussion obtained:1. Excess of PVA composition from polymer absorption spectrum pattern plasticizer.2. The compatibility of PVA, PVC and Plastisizer compositions can reduce the polymer absorption spectrum pattern.

REFERENCE

[1] Apetrei, R. M., Cârâc, G., Bahrim, G. E., (2015), Bioproduction and Relevance of Conducting Polymers : Polypyrrole, Innovative Romanian Food Biotechnology Vol. 17, Issue of November, 2015, © 2015 by Galati University Press, *Review Article*.

[2] Barbosa, A.R., Karmali, A., (2011), Development of a biosensor for urea assay based on amidase inhibition using an ion-selective electrode, Original Article, *Biocatalysis and Biotransformation,* July–August 2011; 29(4): 130–140, ISSN 1024-2422 print/ISSN 1029-2446 online © 2011 Informa UK, Ltd :DOI: 10.3109/10242422.2011.591926.

[3] Broncová, G., Shishkanova, T. V., Krondak, M., Volf, R., and Král, V., (2008), Optimalization of Poly(neutral red) Coated-wire Electrode for Determination of Citrate in Soft Drinks, *Sensors* 2008,*8*, 594-606, ISSN 1424-8220, © 2008 by MDPI, www.mdpi.org/sensors.

[4] Dey, D., and Goswami T, (2013), Thin film Based Bio-electronic Sensors: Future Generation of Electronic Sensor Technology, Journal of current research in science (ISSN 2322-5009), CODEN (USA): JCRSDJ, 2013, Vol. 1, No. 4, pp:199-204, Available at www.jcrs010.com, Original Article.

[5] Faridbod, F., Ganjali, M.R., Dinarvand, R., Norouzi, P., (2008), Development in the Field of Conducting and Non-conducting Polymer Based Potentiometric Membrane Sensors for Ions Over the Past Decade, Sensors, 2331-2412, ISSN 1424-8220.

[6] Han, W.,S , Hong, T. K., Lee, Y. H., (2011), Thiocyanate Ion Selective Solid Contact Electrode Based on Mn Complex of *N*,*N*'-BIs-(4-Phenylazosalicylidene)-O-Phenylene Diamine Ionophore, *American Journal of Analytical Chemistry*, 2011, 2, 731-738 doi:10.4236/ajac.2011.26084 (http://www.SciRP.org/journal/ajac).

[7] Jaworska, E., Maksymiuk, K., and Michalska, A., (2015), Carbon Nanotubes-Based Potentiometric Bio-Sensors for Determination of Urea, *Article,* Chemosensors 3, 200-210; doi:10.3390/chemosensors3030200, ISSN 2227-9040.

[8] Krajewska, A., Lhotak, P., Radecka, H., (2007), Potentiometric Responses of Ion-Selective Electrodes Dopped with Diureidocal[4]arena towerds Un-dissociated benzoic Acid, Full Research Paper, Sensor, 7, 1655-1666, ISSN 1424-8220.

[9] Mansur, H. S., Palhares, R. M., Andrade, G. I., Mansur, A. A. P., and Stancioli, E. F. B., (2008), Improvement of viral recombinant protein-based immunoassays using nanostructured hybrids as solid support, J Mater Sci: Mater Med (2009) 20:513–519, DOI 10.1007/s10856-008-3606-z, Springer.

[10] Mignardi, S., Corami, A., Ferrini, V., (2013), Immobilization of Co and Ni in Mining-Impacted Soils Using Phosphate Amendments, Water Air Soil Pollut (2013) 224:1447, DOI 10.1007/s11270-013-1447-y, Springer.

[11] Mohammadi, M., Khodadadian, M., and Ofouei, M. K. R., (2010), Novel Palladium(ii) Selective Membrane Electrode Based on 4-[(5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl]benzene-1,3-diol, Novel Palladium(II) Selective Membrane Electrode, Collect. Czech. Chem. Commun. 2010, Vol. 75, No. 5, pp. 563–575.

[12] Niu X, Wang Z, Li Y, Zhao Z, Liu J, et al. (2013) ''Fish-in-Net'', a Novel Method for Cell Immobilization of Zymomonas mobilis. PLoS ONE 8(11): e79569. doi:10.1371/journal.pone.0079569, November 2013 Volume 8 Issue 11 e79569. PLOS ONE | www.plosone.org

[13] Niu, H. Y, Lang, W. Z., Liu, Y. X., and Guo, Y. J., (2013), Pervaporation Separation of Dimethyl Carbonate/Methanol Binary Mixtures with Poly(vinyl alcohol)-perfluorslulfonic Acid/poly(acrylonitrile) Hollow Fiber Composite Membranes, Fibers and Polymers 2013, Vol.14, No.10, 1587-1594, DOI 10.1007/s12221-013-1587-0.

[14] Othman, A.M., Houseini, M.E., (2011), Potentiometric determination of α-L-fucosidase enxyme by using 2-chloro-4-nitrophenol-rhodamine B ion pair chemical recognition in PVC membran sensors, Anal Bioanal Chem, 787-795; doi :10.1007/s00216-011-4774-0, Springer.

[15] Schönauer, D., Fleischer, M., and Moos, R., (2013), Half-Cell Potential Analysis of an Amonia Sensors with the Electrochemical Cell Au|YSZ|Au, V_2O_5-WO_3-TiO_2, Sensors, 4760-4780; doi: 10.3390/s130404760, ISSN 1424-8220.