Determination of Formaldehyde using Sensor Formaldehyde

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Abstract: Determination of formaldehyde using sensor formaldehyde. The aim of this study was to make SPCE-based formalin sensors using cellulose acetate as ionophore by studying the effect of pH, response time and its application on salted fish samples. The results showed that the formalin sensor gave the optimum measurement results at the pH of the solution at 4 with a response time of 10 seconds. The results of measuring formalin in salted fish using sensors compared to the spectrophotometric method gave results that were not significantly different.

Key words: ion selective electrode, formaldehyde sensor, Screen Printed Carbon Electrode (SPCE).

1. Introduction

Formalin is a trade name for formaldehyde solution 36-40%. Addition of formaldehyde to food in addition to having a low price, formalin has the function of eradicating various types of bacteria, one of which is spoilage bacteria so that it can cause food to last longer and last longer1). The impact of excessive use of formalin on the body will cause interference with organs and systems that exist in the human body. Seeing the dangers that can be caused from the use of formaldehyde, the government through the Regulation of the Minister of Health of the Republic of Indonesia No.722 / MenKes / Per / IX / 88 prohibits the addition of formaldehyde to food even though in practice there is still a lot of food circulating in the community and containing harmful formalin2.

Many methods have developed and are used to perform formal and quantitative analysis of food formalin. Quantitative analysis methods commonly used to determine formalin levels are spectrophotometric methods. The use of this method requires chromotropic acid reagent (1,8-dihydroxynaphthalene-3,6-disulfonic acid). The spectrophotometer-based observation process requires several process steps, including: the stages of formalin separation from food samples, formation of purple dibenzoxantilium cation complex with

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chromotropic acid and observation using a spectrophotometer at a wavelength of 580 nm. This spectrophotometric method has good selectivity and sensitivity in measuring formaldehyde levels in food, but if it is to be used as a routine analysis and used for field analysis, it is more necessary to use portable sensors.

One method that can be used as an alternative choice is an ion selective electrode based on potentiometric methods. Measurement of Formalin in food using ESI has been done by (Sutrisno, 2009) and (Dewi, 2009) which made ESI-based tube type formaldehyde sensors and type of coated wire active with aliquat 336, the results obtained from Nernstian values ranged from 44-48 mV / deck, with a concentration range measuring 10-1 -10-4 M and a life time of less than 30 days. Both use the same membrane composition, namely aliquat 336 as active ingredients, PVC and DOP as support. ESI is three dimensional in shape so that it is less practical to use so that a formal form factor based on SPCE (Screen-Printed Carbon Electrode) is needed which has a two-dimensional shape so it is more practical.

Formalin sensors are based on ion selective electrodes that use the principle of potentiometry, which measures the potential difference in the inner membrane surface with the outer membrane surface. The sensor performance parameters include pH and response time. Therefore, the effect of pH and response time on the formation of formalin sensors will be studied in this study. Furthermore, the validity test of the formalin sensors that have been made is compared with the spectrophotometric method in salted fish samples.

2. Experimental

2.1 Tools and Materials

The equipment used in this study include: apparatus glass, magnetic stirrer, pH-meter, screen printed carbon electrode plat, spectrophotometer UV Vis, digital multimeter.

The materials used include: cellulose acetate obtained from rice straw, acetone, formaldehyde, phosphoric acid, natrium thiosulfate, kromatopic acid, sulfuric acid, Chloride Acid (HCl), Natrium Hydroxide (NaOH), mercury sulfate (HgSO₄) and aquadest.

2.2 Research Procedure

Preparation of formaldehyde sensor

A solution is made: 0.1 g of cellulose acetate plus 5 mL of 90% ethanol, stirred for 24 hours, then a solution of B: 0.1 g of formalin is dissolved in 10 mL of phosphate buffer pH = 9 and coated onto the SPCE surface, then dried.

The effect of pH

The effect of the pH of the test solution was carried out by measuring the potential of formalin solution with a concentration range of 1-10 ppm in the pH range 4 - 12 for 3 repetitions.

Response time

Each test solution was pipetted as much as 25 mL, then measured its potential at each concentration with an interval of 10-180 seconds, measurement interval every 10 seconds to show a fixed potential price, from the observations will be made a graph of the potential relationship generated for each concentration compared to the observation time every 10 seconds.

3. Result and Discussion

3.1 The effect of pH

The effect of pH on the performance of formic ESI carried out by measuring the potential CHOONa solution concentration of 10⁻⁸-10⁻¹⁰ M at pH 3-9 is shown in Figure 1. Referring to Figure 1 shows the changes in the results of the research formic ESI produced have optimum performance in the pH range 4 because in the pH range the performance of the formic ESI produced is close to the theoretical Nernst price.
Figure 1. The relationship between pH and Nernstian value

3.2 Response time

Response time is the time needed to achieve equilibrium between formic ions in solution with formic ions in the membrane at each measurement of formalin solution until each shows a constant cell potential price. Equilibrium occurs at the interface of the solution with the membrane, where in the reaction process there is an exchange between the formic ion in the solution and the formic ion which is at the membrane interface using cellulose acetate. When the ion exchange reaches equilibrium, the potential price will be constant. Determination of response time is done by making a curve of the relationship between the time of measurement of the cell potential (Ecell), which is shown in Table 1 and Figure 2.

Table 1. Time response of formaldehyde sensor

| [formaldehyde] (M) | p [formaldehyde] | Response time (second) |
|--------------------|------------------|------------------------|
| 1 x 10⁻¹           | 1                | 30                     |
| 1 x 10⁻²           | 2                | 50                     |
| 1 x 10⁻³           | 3                | 30                     |
| 1 x 10⁻⁴           | 4                | 50                     |
| 1 x 10⁻⁵           | 5                | 30                     |
| 1 x 10⁻⁶           | 6                | 60                     |
| 1 x 10⁻⁷           | 7                | 80                     |
| 1 x 10⁻⁸           | 8                | 90                     |
Based on Table 1 and Figure 2 it can be seen that the more concentrated the solution, the faster the response time is up to 30 seconds at a concentration of $10^{-1}$ M, 50 seconds for concentrations of $10^{-2}$ M, and 30 seconds at concentrations of $10^{-3}$ M and 50 seconds at concentrations of $10^{-4}$ M. This is because the concentrations of more concentrated solutions contain more formic ions, consequently the mobility of ions in the solution also increases compared to those with low concentrations so that the time needed by the membrane to reach equilibrium is faster. This response time is included in the ideal sensor category, which has a response time of <1 minute. These results indicate that the speed of ion association formation after reaction after ion exchange is rapid.

3.3 Validity test

The performance of formaldehyde sensors needs to be validated by the standard method of the visible beam spectrophotometer to determine whether the sensor method and standard method are significantly different or not. The measurement data using formalin sensors and standard methods in salted fish samples are shown in Table 2.

Table 2. Formalin levels in salted fish samples

| sample | Concentration (ppm) using spectrophotometric methods | Concentration (ppm) using formaldehyde sensor |
|--------|------------------------------------------------------|----------------------------------------------|
| A      | 1.31                                                 | 1.45                                         |
| B      | 2.09                                                 | 2.09                                         |
| C      | 2.98                                                 | 3.10                                         |

Table 3. Comparison of formaldehyde measurements using sensors and spectrophotometer

| Concentration (ppm) | spectrophotometer | sensor | $T_{meas}$ | $T_{table}$ |
|---------------------|-------------------|--------|------------|-------------|
| 1                   | $1.31 \pm 2.55 \times 10^{-3}$ | $145 \pm 1.73$ | -0.141      | 3.182       |
| 2                   | $2.09 \pm 2.12 \times 10^{-3}$ | $2.09 \pm 1.58$ |            |             |
| 3                   | $2.98 \pm 2.23 \times 10^{-3}$ | $3.10 \pm 0.71$ |            |             |
Based on Table 3 it can be seen that the results of measurements of formaldehyde levels using spectrophotometric and sensor methods yield results that are not much different. This indicates that the potentiometric method based formaldehyde sensor has a fairly good measurement accuracy. According to Gandjar, et al (2008) regression correlation tests need to be done to determine whether formaldehyde sensors based on potentiometric methods can be used as an alternative method of measuring formaldehyde levels. If \( r \text{count} > r \text{table} \) then it is stated that there is a correlation between the standard method \( (x) \) and the potentiometric method \( (y) \). This regression correlation test is shown in Equation 1.

4. Conclusion

The manufacture of formaldehyde sensor has been succeeded. The formalin sensor made has optimum performance at the pH of the solution of 4 with a response time of 10 seconds. The results of formaldehyde measurements in salted fish samples using formaldehyde sensors gave no significant difference when compared with spectrophotometric methods.

References

1. Fadholi, S., 2008. *Formaldehyde in Foods*. Kompas Press. Jakarta
2. Gandjar, I. G., Rohman, A. 2008. *Pharmaceutical Chemistry Analysis*. Pustaka pelajar : Yogyakarta.
3. Judarwanto, W. 2006, *The effect of Formaldehyde for Immune Body*. R.S Husada. Jakarta.
4. Koswara, S. 2006. *Mengawetkan Tahu Tanpa Formalin*. Departemen Ilmu dan Teknologi Pangan Institut Pertanian Bogor. Bogor
5. Laksminarayanaiah, N. 1976. *Membrans elektrodas*. Academic Press : London.
6. Choi, Y.W dan S.H, Moon, 2004. *Determination of Cr(VI) using Ion Sective Electrodes with SIMS Containing Alistat 356*. Klower Academic Publisher, 163-178.
7. Cobben, et al. 1992. *Transduction of Selective Recognition of Heavy Metal Ions by Chemically Modified Field Effect Transistors (CHEMFETs)*. J. Am Chem Soc. 144: 10573-10582.
8. Gao, Y. M, Oshima, S. Motomizu. 2000. *Adsorptions Bahavior of Metal Ions on Cross-linked Chitosan and the Determination of Oxabions after Pretreatment with a Chitosan Column*. In. Analytical Sciences Volume : 16
9. Gea, S. 2000. *Pemabuatan dan Karakterisasi Membran Pb\textsuperscript{2+}- Kitosan Sebagai Sensor Kimia*. Magister PPs USU. Medan : Medan.
10. Gupta, V.K, Jain, A.K and Gaurav Maheshwari. 2007. *Synthesis, Characterization and Pb(II) Ion Selectivity of N, N’-bis(2-hydroxy-1-napthalene)-2,6-pyridiamine (BHNPD)*. International Journal of Electrochemical science.
11. Shamsipur, M., Kazemi, S. Y., Shanghi, H., 2007. Design of a selective and Sensitive PVC-membrane potentiometric sensor for strontium ion based on 1,10-diazo-5,6-benzo-4,7-dioxacyclohexadecane-2,9-dione as a neutral ionophore, Journal of Sensor. 7 : 438-447.
12. Skoog, et al. 1998. *Fundamental at Analytical Chemistry*. Saunders Collega Publishing : Philadelphia.
13. Umezawa et al. 2000. *Potentimetric Selectivity Coefficients of Ion-Selective Electrodes Inorganic Cation Part i, Pure & Appl. Journal of Chem. 72 : 185-190.
14. Vasely, J.W, Daliboi dan S, Karel. 1978. *Analysis with Ion Selective Electrodes*. Ellis Horwood Limited Publisher : Chilchester.

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