

The Studies on the Development of Ion-Selective Electrode for the Determination of Food Colours

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〈Abstract〉

The present study described work carried out in a search for a satisfactory PVC electrode for use in the determination of food dyes. PVC electrodes based on bismark brown-sunset yellow FCF and on bismark brown-amaranth have been found to give useful titration curves for the titration of acid food dyes with bismark brown.

The electrode with the solvent mediator, 2-nitrophenyl-n-butyrate showed the better response than the others to the dye concentration. Short life of the electrode was the main drawback and it would be caused by the decomposition of the mediator.

식용 색소농도의 정량을 위한 Ion-Selective Electrode의 개발에 관한연구

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〈요 약〉

본 연구는 식용색소의 정량분석에 사용하기 위한 PVC 전극의 개발을 위하여 수행된 사항들을 기술하였다. Bismark brown-sunset yellow FCF 및 bismark brown-amaranth를 사용하여 제작한 PVC 전극들은 식용색소의 정량에 유용하게 사용될 수 있는 적정 곡선을 보였다. 2-nitrophenyl-n-butyrate를 매체로 사용한 전극은 다른 매체를 사용했을 때 보다 색소농도에 대한 반응성이 더욱 좋았었다. 전극의 수명이 짧은 것이 큰 단점이었으며, 이것은 매체가 분해되어 생긴 현상이라고 생각된다.

I. Introduction

The ion selective electrodes applied to a range of membrane electrodes which respond selectively toward one or several ionic species in the presence of others were not proceeded until about 1966(2). Several thousands of papers on this subject, however, published in the late 1960's (3).

The most comprehensive reviews are those of Buck (4,5), Covington(3), and Koryta(6). The book written by Moody and Thomas(7) and

others(8-12) cover both theoretical and practical aspects of ion selective electrodes.

It is worth knowing that Nicolsky(8) first presented the form of the Nernst equation which describes the response of a hydrogen ion-selective electrode to both hydrogen and sodium ions.

$$E = E_0 + \frac{2.303RT}{nF} \log_{10}(a_{H^+} + K_{HNa} \cdot a_{Na^+})$$

where E is the electrode potential in the solution containing both ions, E^0 is the standard potential of the electrode, and R , T , and F have their conventional meanings. a_{H^+} , a_{Na^+} , and K_{HNa}

Table.1 Food dyes permitted to use in Korea

NO	Colour Index Name	Commercial Name	Structure
1	Food Green No 3	Fast Green FCF	
2	Food Red No 2	Amaranth	
3	Food Red No 3	Erythrosine	
4	Food Blue No 1	Brilliant Blue FCF	
5	Food Blue No 2	Indigo Carmine	
6	Food Yellow No 4	Tartrazine	
7	Food Yellow No 5	Sunset Yellow FCF	

are the activities of hydrogen ion and sodium ion, and selectivity coefficient respectively.

In general the equation for any cation(a_M) or anion(a_X), the Nernstian potential-activity response can be given respectively as

$$E = E^0 + \frac{RT}{nF} \ln a_M$$

$$E = E^0 - \frac{RT}{nF} \ln a_X$$

The dyes which are used in food, clothing, and cosmetics must be harmless as we touch them in our daily lives. As a result of the responsibilities of the Food and Drug Administration in the U.S.A. or its counterparts in other countries, dyes have been examined with respect to their safety, particularly from the viewpoint of carcinogenity. A work has been reported on the chronic toxicity of 4 certified food colourings, amaranth, tartrazine, new cocine and sunset yellow, in rats(15). The results indicated that female rats may be more sensitive to some synthetic coal-tar dyes than males as far as effect on growth is concerned.

The dyes permitted to use in food in this country are listed on Table 1 excluding their corresponding lakes.

A few attempts have been made to determine acid and basic dyes using liquid state ion-selective electrodes by Fogg et al (1,13). The electrode body used for those studies has been described previously(14).

The present work has been concerned with the determination of food dyes, potentiometrically. The PVC membrane electrode was prepared by sticking the PVC membrane formed at the end of glass tube and by inserting the silver/silver chloride reference electrode in the glass body. The PVC membrane incorporating sensors such as bismark brown-sunset yellow FCF and bismark brown-amaranth should contain plasticizer and solvent mediator. The electrodes were shown to be useful as indicator electrodes in the titration of some acidic food

dyes with standard solution of reactants.

II. Experimental

The PVC membrane electrodes were prepared according to the methods of Craggs, Moody and Thomas(16). 0.15g of sensing material, i.e. bismark brown-amaranth, bismark brown-sunset yellow FCF, was dissolved in 2 to 3 drops of solvent mediator such as 2-nitrophenyl-n-butylate, p-nitrotoluene and squalane or trixylenyl phosphate, mixed with 2 to 3 drops of plasticizer (di-nonylphthalate or n-butylphthalate), and finally mixed thoroughly with 6ml of tetrahydrofuran solution containing 0.15g PVC(KH -10 or VAGH) powder. The homogeneous mixture was poured onto a glass ring (3.6cm i.d.) on a flat glass plate. A flexible PVC membrane is cured within a couple of days and has the thickness between 0.2 and 0.4mm. A circular PVC membrane was cut out from the prepared master membrane using a cork borer No.8 and stuck on one end of a glass tube using a glue solution prepared by dissolving polyurethane in tetrahydrofuran. The PVC membrane electrode was completed by dipping the silver/silver chloride internal reference electrode in the glass tube containing 1M potassium chloride solution. Several electrodes were prepared using different sensors, solvent mediators, and plasticizers as shown in Table 2.

The slightly soluble compound, bismark brown-sunset yellow FCF was prepared by adding 100ml of sunset yellow FCF aqueous solution including 0.5g of pure solid sample into 100ml of 0.01M bismark brown solution at 70°C with continuous stirring. The precipitate was washed with water by decantation over a period of several hours and was filtered finally onto a No 4 glass filter and washed with water until colourless washings were obtained. The precipitate was dried in a vacuum oven at 70°C

Table.2 The composition of the PVC membrane electrodes.

components		No. of electrodes	E1	E2	E3	E4
bismark brown sunset yellow FCF(g)			0.15	0.15	—	—
bismark brown amaranth(g)			—	—	0.15	0.15
2-nitrophenyl-n-butyrate(ml)			—	0.20	—	0.20
tetrahydrofuran(ml)			6	6	6	6
PVC powder	KH-10		0.15	0.15	—	0.15
	VAGH		—	—	0.15	—
p-nitrotoluene(g)			0.07	—	0.03	—
di-n-butyl phthalate			2 drops	—	2 drops	—
squalane (drops)			2	—	—	—
trixylenyl phosphate(g)			—	—	0.04	—
di-nonylphthalate(ml)			—	0.20	—	0.20

for 1 hour. Bismark brown-amaranth compound was also prepared by the similar procedure described above. The yield of bismark brown-sunset yellow FCF and bismark brown amaranth was 0.42g and 0.58g respectively.

The potential measurement was carried out by using the pH meter (EIL 46A vibret). A saturated potassium chloride agar bridge was connected to a saturated calomel reference electrode (SCE). All potentials were recorded versus the SCE.

Food dyes used were reagent grade provided by Beecham products Ltd. PVC powder for the inert matrix of the membrane was the product of Korea Plastic co. All the other chemicals used here were reagent grade and used as they were.

III. Results and Discussion

PVC matrix electrode based on the sensor bismark brown-sunset yellow FCF and bismark brown amaranth gave a response less than Nernstian. The response to sunset yellow FCF and amaranth, for example, was 40mV per decade in the range $10^{-2}M$ down to $10^{-6}M$.

More reproducible and stable potential values could be obtained with a potassium chloride agar bridge connected to the reference electrode, SCE than dipping the SCE directly into the solution to be measured. A bigger potential fluctuation normally resulted in the latter case. The response of the electrode to the same concentration of the species was not perfectly constant all the time due to changes in the junction potential, the position of the electrode in the solution and the stirrer speed. The application of the electrodes to the potentiometric titration of food dyes, however, was shown to give quite successful results. Fig.1 shows some of the potentiometric titration results for the sunset yellow FCF and amaranth with a standard bismark brown solution using the electrode E2 and E4 respectively. A big potential jump which was taken to be the end point was obtained with new membrane electrodes. Using the same electrode over again in the same system as well as a different system (old membrane) the potential jump was remarkably decreased. It is noteworthy to mention that the steepest portions of the titration curves are the

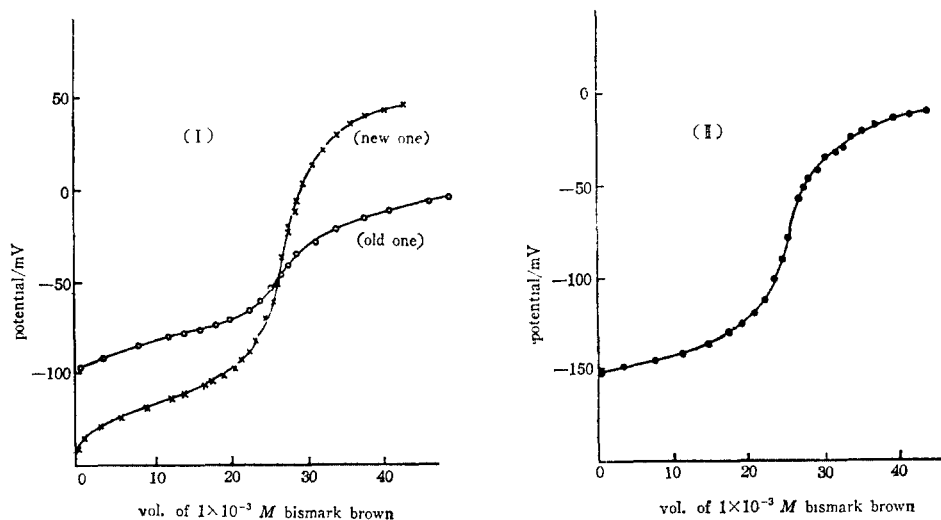


Fig.1 Potentiometric titration curves of 25ml of $1 \times 10^{-3}M$ (I) sunset yellow FCF, (II) amaranth using E2 and E4 electrode respectively.

same for both electrodes, i.e. new and aged electrodes. More significant result would be expected from the titration work than the direct measurement of the potential. The electrode was not so greatly influenced by pH changes between 5 and 9 in the dye solution.

The response time of the new membrane electrodes E2 and E4 to sunset yellow FCF and amaranth as well as bismark brown was fast such as 20 seconds. The deteriorating phenomenon of those PVC electrodes appeared as a smaller Nernstian factor for the species to be measured as time went by. The solvent mediator, 2-nitrophenyl-n-butyrate was decomposed so quickly that the electrode can not last longer than 10 days. The behaviour of electrodes E1 and E3 was even worse than E2 and E4. Any viscose chemicals with the character of sufficient stability and of solubility of the sensor would improve the membrane electrode to have long life.

Further studies should be carried on the improvement of the electrode and the effect of interferences.

IV. Conclusion

Bismark brown-sunset yellow FCF and bismark brown-amaranth have been used as a sensor for the determination of food dyes using the PVC membrane electrodes. The potentiometric titration curves for food dyes with bismark brown using the electrode E2 and E4 showed reasonably good features, but they were rather diffuse owing to the high solubility of the product.

The short life of the electrode due to the use of solvent mediator would be the main drawback of the electrode.

The present work, however, has provided a useful method for the determination of dyes using the ion-selective electrodes.

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References

1. A. G. Fogg, A. A. Al-Sibaai and K. S. Yoo, *Analyst. Letters*, 10, 173 (1977).
2. R. A. Durst, ed., *Ion Selective Electrodes* NBS Spec. Publ. 314, U.S. Gov. Printing Office, Washington, D.C. (1969).
3. A. K. Covington, *Critical Reviews in Analytical Chemistry*, 3, 355 (1974).
4. R. P. Buck, *Anal. Chem.*, 48(5), 23R(1976).
5. *ibid.*, 50(5), 17R(1978).
6. J. Koryta, *Anal. Chim. Acta*, 91, 1(1977).
7. G. J. Moody and J. D. R. Thomas, *Selective Ion Sensitive Electrodes*, Merrow, England (1971).
8. P. L. Bailey, *Analysis with Ion-Selective Electrodes*, Heydon, London (1976)
9. G. E. Baiulescu and V. V. Cosofret, *Applications of Ion-Selective Membrane Electrodes in Organic Analysis*, Ellis Horwood Ltd. Pub. (1977)
10. J. Koryta, *Ion-Selective Electrodes*, Cambridge Univ. Press(1975).
11. N. Lakshminarayanaiah, *Membrane Electrodes*, Academic Press (1976).
12. H. J. Berman and N. C. Herbert ed., *Ion-Selective Microelectrodes*, Plenum Press(1974).
13. A. G. Fogg and K. S. Yoo, in *Ion Selective Electrodes* ed. by E. Pungor, p369, Budapest Conference, Sept. 5—9, 1977, Elsevier Scientific pub. co. (1978).
14. A. G. Fogg, M. Duzinkewycz and A. S. Pathan, *Anal. Letters*, 6, 1101(1973).
15. J. K. Lin, S. S. Sung, K. H. Ling, R. B. Lee, and S. S. Chang, *Procs. Natl. Sci. Council, Repub. China*, 1(11), 46(1977).
16. A. Craggs, G. J. Moody and J. D. R. Thomas, *J. Chem. Educ.*, 51, 541 (1974).