

Aliquat336이 함침된 고분자막 이온선택성 전극을 이용한 Cr(VI) 측정에 관한 연구

최영우, 문승현

우 50-712, 광주광역시 북구 오룡동 1
광주과학기술원 환경공학과 청정분리연구실

Determination of Cr(VI) by using a polymeric membrane ion selective electrode with Aliquat336

Young-Woo Choi, Seung-Hyeon Moon

Department of Environmental Science and Engineering,
Kwangju Institute of Science and Technology,
1 Oryong-Dong, Buk-Gu, Gwangju, Korea, 500-712,
E-mail: shmoon@kjist.ac.kr

1. Introduction

Cr(VI) is one of the hazardous heavy metals monitored in water and wastewater streams. In previous studies, the application of ion selective electrodes (ISEs) for determination of Cr(VI) was investigated using tetrakis (thiocyanato) chromate and diphenylguanidine as electroactive substances. However, the electrodes had some drawbacks, such as inadequate selectivity, short lifetime, poor reproducibility in preparation, potential drift, and long response time.

In this study, a liquid membrane was employed for selective measurement of Cr(VI). Supported liquid membranes (SLMs) have advantages in terms of ease of the membrane preparation and controllability of the membrane selectivity. ISEs for ionic materials have been widely used with the poly(vinyl chloride) homopolymer containing appropriate carriers. Tricaprylmethyl ammonium chloride (Aliquat336) has been shown to be an effective extractant for separation and

purification of a number of metals because of its excellent chemical stability and low solubility in water. Particularly, Aliquat336 was reported to be highly selective for the extraction of Cr(VI). The objective of this study is to develop Cr(VI) sensor with Aliquat336-embedded SLMs.

2. Theory of ISE

The emf signals of an ISE are manifested qualitatively by the change in capacity of the double layers made within the boundary layer of a sample phase. A modified Nicolski-Eisenman equation used for determining Nernstian slopes experimentally as shown in equation (1).

$$E = E_0 + \frac{RT}{nF} \ln(a_1 + \sum_{i=2}^q K_{1i}^{z_i/z_1} a_i^{1-z_i/z_1} a_i) \text{-----(1)}$$

The fraction of chromate species in a solution depends on the pH according to the equilibrium relations. pH range of 3 to 6, HCrO_4^- and the orange-red dichromate ion CrO_4^{2-} are in equilibrium. In this study, the predominant chromate species is HCrO_4^- .

3. Experiment

The poly(vinyl chloride) was used as a base matrix for preparing SLMs. Aliquat336 was used as a carrier for the selective detection of Cr(VI), and *o*-nitrophenyl octyl ether (NPOE) was used as plasticizer to provide mobility for the carrier. Tetrahydrofuran (THF) was used as solvent for mixing the membrane materials. To measure electromotive forces of Cr(VI) and interferences, a working and a reference electrode were used; one is constituted by a SLM with an inner filling solution, $1\text{E-}4 \text{ M K}_2\text{Cr}_2\text{O}_7$ and KCl and the other by Ag/AgCl with a saturated KCl solution. Selectivities for Cr(VI) and interferences were calculated by the fixed interference method (FIM) and the separate solution method (SSM) recommended by IUPAC. Detection limit of Cr(VI) in presence of interferences were obtained by FIM. And also a long term stability of the prepared ISE was tested for applying to continuous monitoring of waste stream.

4. Results and Discussion

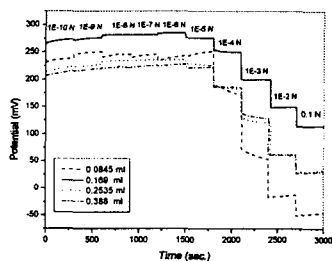


Fig. 1. Emf as a function of Cr(VI) concentration for ISE membranes with the various concentration of Aliquat336 as an carrier with 1.0 ml of NPOE

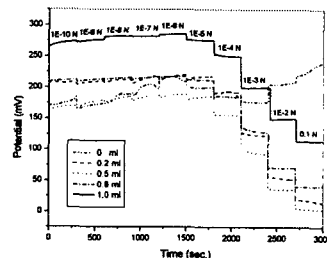


Fig. 2. Emf as a function of Cr(VI) concentration for ISE membranes with the various concentration of NPOE as a plasticizer with 0.169ml of Aliquat336

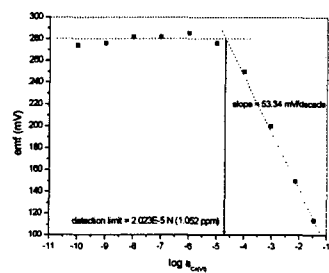


Fig. 4. Emfs as a function of the various conc. of the primary ion with the inner filling solution of respective $1E-4$ M of $K_2Cr_2O_7$, KCl

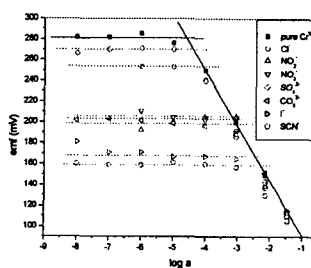


Fig. 5. Effect of interferences with respect to the various conc. of Cr(VI) by a fixed interference method; respective 0.01 M of interfering ions was added in test solutions and concentration of the inner filling solution was respective $1E-4$ M of $K_2Cr_2O_7$, KCl

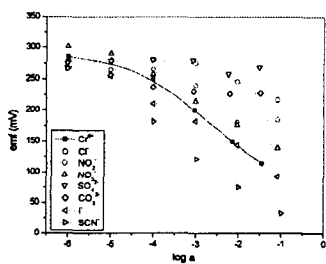


Fig. 5. Effect of interferences with respect to the various conc. of Cr(VI) by a separate solution method; concentration of the inner filling solution was respective $1E-4$ M of $K_2Cr_2O_7$, KCl

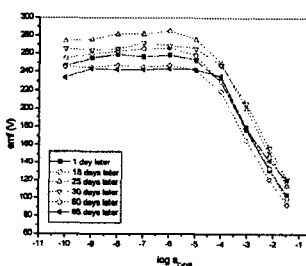


Fig. 6. Calibration curves of Cr(VI) for long term stability with a batch detection using a ISE membrane impregnated with 0.5 g PVC/ 1 ml NPOE/ 0.169 ml Aliquat336 and also with the inner filling solution of respective $1E-4$ M of $K_2Cr_2O_7$, KCl

It was clarified that the ISE membrane impregnated with Aliquat336 responded entirely to monovalent anionic species of chromate, HCrO_4^- , in spite of the wide detection range of Cr(VI) from about 1 ppm to over 5000 ppm. An ISE for stable sensitivity and long term stability was optimized with the SLM impregnated with 0.5 g PVC/ 1 ml NPOE/ 0.169 ml Aliquat336. To investigate the effect of interfering ions on the detection limit and the selectivity, the fixed interference method (FIM) and the separate solution method (SSM) recommended by IUPAC were used and the results showed that the ISE used in this study was higher Cr(VI) selective against the interferences as an order of $\text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{Cl}^- > \text{NO}_2^- > \text{NO}_3^- > \text{I}^- > \text{SCN}^-$. It is expected that the lower detection limit of ISEs can generally be improved by partially replacing the primary ions at the inner membrane surface with change of composition of the inner filling solution. A stable response of Cr(VI) using the optimized ISE was obtained within 1 sec. detection time during at least over 2 months with a batch detection. Therefore, it is suggested that this ISE is not only adaptable for potentiometric measurement of Cr(VI) ion but feasible and reproducible for continuous monitoring of Cr(VI) in waste stream.

Acknowledgements

This work was supported by the National Research Laboratory (NRL) Program of Korea Institute of Science and Technology Evaluation and Planning (Project 2000-N-NL-01-C-185).

References

1. Albrecht Uhlig et al., *Anal. Chem.*, Vol. 69(19), pp. 4032-4038, 1997
2. E. Bakker, *Electroanalysis*, Vol. 9, No. 1, p. 8, 1997
3. Y. W. Choi et al., *J. of KARP*, Vol. 24(1), p. 11, 1999
4. V. M. Rudoj et al., *J. Anal. Chem.*, Vol. 53, No. 2, pp. 144-146, 1998
5. T. Sato et al., *J. Appl. Chem. Biotech.*, 23, pp. 909-917, 1973
6. T. Sekine et al., *Solv. Extr. Ion Exch.*, 7, pp. 73-86, 1989
7. R. K. Tandon et al., *Talanta*, 31, p. 227, 1984