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Dynamic Calibration and Memory Effect for Fluoride Ion Selective Electrode

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Synopsis. The dynamic calibration of the F^- ion selective electrode was briefly evaluated in terms of the memory effect of the electrode by analyzing the NBS urine standard.

Liberti and Pinto[1] reported the "dynamic" calibration for the iodide ion selective electrode, where the electrode response after a selected time is compared with a calibration curve obtained by contacting the electrodes with standard solutions for the same time. Thus we can continuously monitor quickly changing concentrations, although the response is not necessarily rapid. For most of the solid membrane electrodes such as the fluoride ion electrode, the response time is less than 30 s when we define the response time as the time necessary to cover 95% of the equilibrium potential. The 95% attainment of the equilibrium potential involves about 30% error in the concentration at around 10^{-5} M of F^- ions. If we define the response time as the time to reach 0.2 mV pre-equilibrium potential, for example, the resulting error is 0.2% in terms of concentration, but causes much longer response time as shown in Table 1. This result implies that in the case of ordinary analysis, we are inherently using the dynamic calibration procedure, because final potentials are read in several minutes at longest. On the other hand, one of the main factors which affects the accuracy of results for ion selective electrodes at lower concentration range seems to be the "memory effect." Usually, the calibration curve is constructed by changing the concentration from low to high. In most cases, the concentration of the sample is located at around the middle of the calibration curve. This means one has to come back from higher concentration to lower one to measure the analyte concentration in the sample right after making calibration curves. Hence, the electrode inevitably remembers the higher concentrations of the previous runs causing an error in analysis even when the electrode surface is thoroughly rinsed after each run. This would also hold true for continuous analyses where the concentration could change up and down in a short time.

Table 1. Response time for F^- ion selective electrode[a)]

Concn of F^- ion(M)	Response time(min)[b)]
2×10^{-7}	200
5×10^{-7}	40
1×10^{-6}	24
5×10^{-6}	22
1×10^{-5}	18
2×10^{-5}	11
1×10^{-4}	5
1×10^{-3}	2

a) F^- ion selective electrode of DKK. b) Necessary time to reach 0.2 mV pre-equilibrium potential.

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In the present study, the dynamic calibration procedure was briefly evaluated in terms of the memory effect of the fluoride ion selective electrode by estimating the minimum time required for accurate F^- ion determination in the NBS human urine standard as illustrative example for natural samples. If the dynamic calibration works also satisfactorily for the natural systems, it would be extremely useful for clinical or environemental analysis where rapid and continuous measurements are highly desirable.

Experimental

In order to obtain precise and accurate hard copies of the potential *vs.* time profile of the ion selective electrodes, a special experimental set-up was made.[2] The analog output from the ion selective electrode is first converted into frequencies followed by counting, serialization, and finally data acquisition with a minicomputer. The precision of analog to digital conversion is 0.1 mV.

The dried urine fluoride standard sample (NBS SRM No. 2671) was dissolved in TISAB (Total ionic strength adjustment buffer) solution. The TISAB solution was prepared by dissolving 1 M NaCl, 0.25 M CH_3COOH, 0.75 M CH_3COONa, and 0.001 M sodium citrate in 1 litre of deionized and distilled water. The value recommended by NBS for the fluorine content in this solution is $(4.39\pm0.43)\times10^{-5}$ M (reliability 95%). The result of determination of fluoride ion in this NBS sample by fluoride ion selective electrode coincides with the value recommended by NBS. The total fluorine for the same solution by AlF molecular absorption spectrometry in carbon rod furnace[3] coincides with that of ion selective electrodes and of the NBS value within experimental error.[4] It seems that very little matrix effect exists and almost all fluorine containing species are of the form of free fluoride ion in the dissolved NBS standard sample. The magnitude of the error in the NBS value is rather large presumably due to the average of different lots. Thus, each bottle from the NBS probably contains a homogenous sample and the resulting analytical value should have higher precision. The response time of the fluoride ion selective electrode was examined with four electrode specimens, one from TOA and the other three from DKK. It was found that except for one from DKK which exhibited slightly slower response, three showed almost equal response time (Table 1). Therefore, the experiment concerning the memory effect was performed by using two electrode specimens from DKK, both of which gave virtually the same results (Tables 2 and 3).

Chemicals of analytical grade were used. Water was deionized and distilled. Fluoride ion selective electrodes from Denki Kagaku Keiki Co. (DKK) and TOA Dempa Co., Ltd., were used. An Ag/AgCl electrode of TOA Model HS 305 DP was used as a reference electrode. All fluoride ion selective electrodes were rinsed, excess water being wiped off before and after each run. For the dissolved NBS sample, the response time obtained is virtually equal to or slightly shorter than that of the ordinary F^- ion standard solution.

The measurement was performed in a constant temperature bath in a constant temperature room, both thermostated at 20±0.5 °C. The sample solution was stirred with a magnetic stirrer.

Results and Discussion

Table 2 shows the apparent concentration of F^- ions in the NBS standard urine sample obtained through the dynamic calibration curves at different waiting times. We deal with two cases: Analysis of the NBS sample is made after the measurements of 1) 1×10^{-4} M and 2) 1×10^{-5} M of the standard solutions for the calibration curves. The F^- ion concentrations for the NBS sample lies between these concentrations. The apparent concentration of F^- ions obtained in the NBS standard urine sample is initially higher than the NBS value for case 1) and gradually decreases to a nearly steady state value, C_1, in about 9 min. This value is consistent with the NBS value, indicating that the memory effect is completely removed. For actual analyses where the concentration of the analyte is not known, it is not clear whether the error from the memory effect is still involved in the C_1 value. Thus the following experiment corresponding to case 2) was performed. The apparent F^- concentration obtained in the NBS standard is initially lower than that of the NBS recommended value in contrast to case 1, increasing gradually to a steady state value, C_2, in about 6 min. The value is also consistent with the NBS value. From these results, it can be concluded that the most accurate method to remove the memory effect completely is to obtain the value C_0 which lies on the asymptotic line between the two concentration-time profiles, nearly equal to both C_1 and C_2($C_1 \fallingdotseq C_2$). This procedure may be called "double calibration." The memory free accurate result can be obtained when the waiting time exceeds 6—9 min. The lower the concentration of the analyte, the lower the accuracy (Table 3). However, even in the presence of the memory effect, we can still obtain fairly accurate results with a *ca.* 20 % error for 10^{-5} M NBS urine standard solution at a waiting time of 6 s.

Table 2. Determination of F^- ion in NBS urine sample[a] through dynamic calibration procedure for F^- ion selective electrode (see text.)

Waiting time (s)	Analysis A[b] ($\times10^{-5}$ M)	Analysis B[b] ($\times10^{-5}$ M)
6	5.40	3.40
9	5.20	3.65
12	5.15	3.75
15	5.05	3.90
18	4.95	3.85
30	4.90	4.25
60	4.65	4.35
120	4.55	4.40
300	4.50	4.45
420	4.50	4.45
540	4.45	4.45
600	4.45	4.40
1200	4.45	4.45
1800	4.45	4.45
3600	4.35	

a) The NBS value: (4.39±0.43)$\times10^{-5}$ M. b) Apparent concentrations A and B obtained after measurement of 1×10^{-4} M and 1×10^{-5} M, respectively, of standard solutions.

Table 3. Determination of F^- ion in diluted NBS urine sample[a] through dynamic calibration procedure for F^- ion selective electrode

Waiting time(s)	Apparent concn($\times10^{-6}$ M)[b]
30	8.05
60	5.68
300	4.70
600	4.30
1200	4.30
1500	4.25
1800	4.25
2400	4.20
3000	4.15

a) Concentration, one order of magnitude lower than that of Table 2. The same NBS sample but different lot from that of Table 2. b) Obtained after the measurement of 1×10^{-4} M standard solution.

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