

Numerical Considerations on the Accuracy of Spike Method for the Determination of Sodium and Potassium Ion

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(Received September 19, 1968)

The accuracy in a spike method of determining sodium ion using a sodium-selective glass electrode was examined by numerical calculations. The correlation among the precision of measuring instrument, the addition rate of sodium ion and the error of determination was expressed in a diagram, and the lower limit of addition rate for a desired error was determined. The relation between the change in the activity coefficient of sodium ion and the addition rate for various values of error was also expressed in a diagram, and the upper limit of addition rate was suggested by applying the MacInnes convention regarding the ionic activity coefficient. The change in potential gradient ($2.303 RT/T$) due to the variation of temperature within $\pm 0.1^\circ\text{C}$ scarcely influenced upon the error of determination.

The accuracy in a spike method of determining potassium ion using a sodium-selective glass electrode and a potassium-sensitive glass electrode was also examined by numerical calculations. The correlations among the selectivity of potassium-sensitive glass electrode, the concentration ratio of sodium ion and potassium ion in the solution, the addition rate of potassium ion, the precision of measuring instrument, and the error of determination were expressed in diagrams, and the lower limit of addition rate for a desired error was determined.

1. Introduction

Recently, the sodium-sensitive and potassium-sensitive glass electrodes¹⁾ have been developed and utilized in many fields.

The ions which particularly interfere with the measurements of concentration of sodium ion by means of the sodium-responsive glass electrode are hydrogen and potassium ion, but the interference from hydrogen ion can be eliminated by controlling the pH of the solution. Moreover, as a result of improvements on the glass electrode, there are now reported glass electrodes which are 30 to 100 times more selective with respect to sodium ion than potassium ion²⁾. Therefore, it is possible to measure the concentration of sodium ion almost completely selectively with a properly selected glass electrode. However, since the glass electrode essentially corresponds to the ionic activity¹⁾, its application to measurements of the concentration of sodium ion has been accompanied by a difficult task of correcting the ionic activity coefficient.

On the other hand, the interference of sodium ion with the measurements of potassium ion in the electrode method is unavoidable, and glass electrodes which are selective with respect to potassium ion alone have not been developed yet.

To solve the above-mentioned problems, Garrels³⁾ determined sodium and potassium

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ion with the use of an ingenious method which is called the spike method. Although simple apparently, this method is subject to a variety of restrictions in its actual application, and an accurate measurement by this method is not possible without sufficient understanding of these restrictive conditions in advance. In this study, the precision of measuring instruments, the change in the ionic activity coefficient, the effect of electrode characteristics and the others were examined by means of numerical calculations to provide an experimental guide.

2. Principles of spike method

2-1. Determination of sodium ion

If the potential of glass electrode responsive for sodium ion in the sample solution whose molality is m is denoted by E and that in the sample solution to which sodium ion is added in an amount of δ by E' , the following equation³⁾ is obtained as long as there is no cationic error⁴⁾,

$$e = E' - E = \frac{RT}{F} \ln \frac{(m+\delta)\gamma'}{m\gamma} = \frac{RT}{F} \ln \left(1 + \frac{\delta}{m} \right) + \frac{RT}{F} \ln \frac{\gamma'}{\gamma} \quad (1)$$

where γ and γ' are the activity coefficients of sodium ion at concentrations of m and $m+\delta$ respectively, R is the gas constant, F is the Faraday constant and T is the absolute temperature. When δ becomes infinitesimal, γ' can be regarded as equal to γ and Eq. 1 can be expressed as follows.

$$e_m = \frac{RT}{F} \ln \left(1 + \frac{\delta}{m} \right) \quad (2)$$

Consequently, m can be calculated from Eq. 2 by substituting the values of e_m and δ .

2-2. Determination of potassium ion

The potential of glass electrode responsive for sodium ion is given by the following equation,

$$E_1 = E_1^\circ + \frac{RT}{F} \ln m_{\text{Na}^+} \cdot \gamma_{\text{Na}^+} \quad (3)$$

where E_1° is the standard potential of glass electrode and γ_{Na^+} is the activity coefficient of sodium ion.

On the other hand, the glass electrode responsive for potassium ion cannot be said completely selective with respect to potassium ion and shows the $\text{Na}^+ - \text{K}^+$ mixed potential. The potential E_2 of potassium-responsive glass electrode is thus represented by the following equation,

$$E_2 = E_2^\circ + \frac{RT}{F} \ln [m_{\text{Na}^+} \cdot \gamma_{\text{Na}^+} + K m_{\text{K}^+} \cdot \gamma_{\text{K}^+}] \quad (4)$$

where E_2° is the standard potential of glass electrode, and K is a selectivity constant which is dependent upon the kind of glass.

From the standpoint of electrode behavior⁴⁾, Eq.4 corresponds to the ideal behavior, but this equation is often found to describe the behavior satisfactorily for some kinds of glass⁵⁾. Now, a cell (A) is constructed as shown and a pure sodium ion solution whose concentration is equal to that of the sample solution is used as the cell solution.

sodium-responsive glass electrode	solution	potassium-responsive glass electrode	voltage compensator	(A)
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In this instance, the second term in the parenthesis in the right side of Eq.4 can be neglected, and the electromotive force of the cell (A) becomes $E_2^\circ - E_1^\circ$ as long as the voltage of the voltage compensator remains zero. Therefore, if a voltage which is equal in the absolute value to $E_2^\circ - E_1^\circ$ but with the opposite sign is generated in the voltage compensator, the electromotive force of the cell, e , is given by the following equation.

$$e = E_2 - E_1 - (E_2^\circ - E_1^\circ) = \frac{RT}{F} \ln \left[1 + \frac{K m_{K^+} \cdot \gamma_{K^+}}{m_{Na^+} \cdot \gamma_{Na^+}} \right] \quad (5)$$

$$\text{or } m_{K^+} = \left\{ \exp(Fe/RT) - 1 \right\} \cdot \frac{m_{Na^+} \cdot \gamma_{Na^+}}{K \cdot \gamma_{K^+}} \quad (6)$$

Next, the electromotive force of the cell is measured after addition of a small amount (δ) of potassium ion to the sample solution. Similar to Eq.6, the electromotive force (e') can be given as follows,

$$m_{K^+} + \delta = \left\{ \exp(Fe'/RT) - 1 \right\} \cdot \frac{m_{Na^+} \cdot \gamma'_{Na^+}}{K \cdot \gamma'_{K^+}} \quad (7)$$

where γ' is the ionic activity coefficient in the solution to which potassium ion is added in an amount of δ . If δ is infinitesimal, γ' is practically equal to γ and the following relationship can be derived from Eqs. 6 and 7.

$$m_{K^+} = \frac{1 - \exp(-Fe/RT)}{\exp\{F(e' - e)/RT\} - 1} \cdot \delta \quad (8)$$

Consequently, the value of m_{K^+} can be calculated.

3. Accuracy in a spike method of determining sodium ion

3-1. Potential difference generated on glass electrode

If the changes in the activity coefficient are negligible, the potential difference, e_m , which is necessary for calculating the concentration of sodium ion is given by Eq.2. The relationship between e_m and the addition rate (δ/m) at 25°C is shown in Fig.1. As can be seen from Fig.1, the values of e_m become considerably small as the addition rate becomes smaller, and the measuring accuracy of the potential difference should be made higher as the addition rate becomes smaller. In an actual experimental procedure, it will be necessary to add sodium ion in such a manner as to make e_m at least equal to or higher than 1-2 mV, although the effect of the activity coefficient to be described in Section 3-3 should be taken into ac-

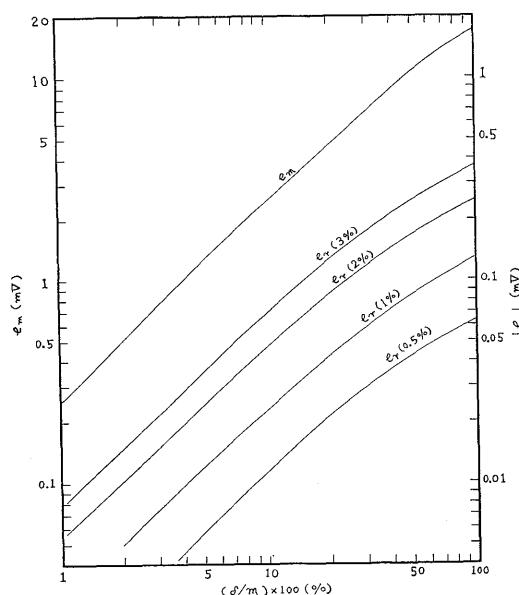


Fig. 1. Relation between e_m and δ/m (Numbers in parenthesis are values of $|\delta m / m| \times 100$).

count.

Furthermore, if e_m is taken as a change in the asymmetry potential of glass electrode, Fig.1 can be used for finding the error of determination due to the change in the asymmetry potential during experiment.

3-2. Precision of potential difference

Differentiation of both sides of Eq. 2 with respect to e_m and m respectively gives the following equation.

$$de_m = -\frac{RT}{F} \cdot \frac{(\delta/m)}{[1+(\delta/m)]} \cdot \frac{dm}{m} \quad (9)$$

Therefore, as long as infinitesimal changes in e_m are considered, Eq. 9 can be expressed as follows at 25°C.

$$\left| \frac{\Delta m}{m} \right| = \frac{\ln 10}{59.15} \cdot \left[1 + \frac{1}{(\delta/m)} \right] \cdot |\Delta e_m| \quad (10)$$

Consequently, the relationship between the measuring accuracy of the potential ($|\Delta e_m|$) and the error of determination ($|\Delta m/m|$) becomes such as is given in Fig. 2.

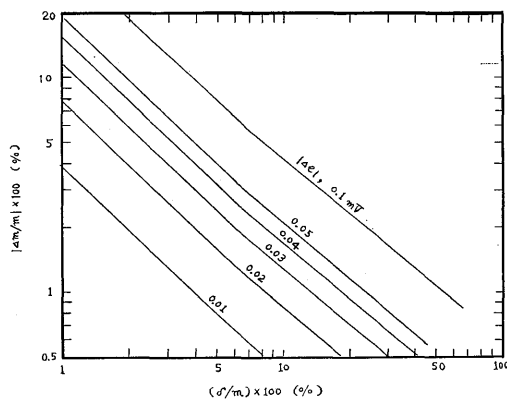


Fig. 2. Relation between $|\Delta m/m|$ and δ/m for various values of $|\Delta e|$.

addition rate above 9% for the expected concentration.

It is to be noted here that the precision of measuring instruments means not the absolute accuracy of the potential but rather the reproducibility. Since e_m is the difference between E and E' , the absolute value of the potential is not necessary, and the good reproducibility is required above all.

For some kinds of glass, the potential gradient of the electrode is not necessarily as the theory predicts, but it is in the range of 58.85–59.15 mV/pNa according to experiences of the author and this difference in the potential gradient does not produce large differences in the results in Fig. 2.

3-3. Effect of activity coefficient

The magnitude of the potential and the precision of instruments indicate an advantage of making the addition rate as large as possible. On the other hand, when the addition rate is too large, changes in the activity coefficient cannot be neglected any more. An allowable limit of the changes in the activity coefficient was calculated as follows.

The potential difference of Eq. 1 to be obtained in practice was used with the assumption that the activity coefficient does not change. Then, the concentration of sodium ion (m') is calculated as shown by the following equation.

$$\ln\left[1+\frac{\delta}{m}\right]+\ln\frac{\gamma'}{\gamma}=\ln\left[1+\frac{\delta}{m'}\right] \quad (11)$$

On the other hand, the relationship of $\Delta m/m=(m'-m)/m=(m'/m)-1=[(\delta/m)/(\delta/m')]-1$ leads to the following equation.

$$\frac{\delta}{m'}=\frac{\delta/m}{1+(\Delta m/m)} \quad (12)$$

Consequently, by putting $\log(\gamma'/\gamma)=\Delta\log\gamma$, the following equation is derived from Eqs. 11 and 12.

$$|\Delta\log\gamma|=\log\left[1+\frac{\delta/m}{1+|\Delta m/m|}\right]-\log\left[1+\frac{\delta}{m}\right] \quad (13)$$

Therefore, once the desirable level of errors is established, Eq.13 will allow the calculation of the limits of changes in the activity coefficient which do not cause the errors to exceed this level for each addition rate. The results are shown by the solid lines in Figs. 3 and 4. To keep the error of determination due to changes in the

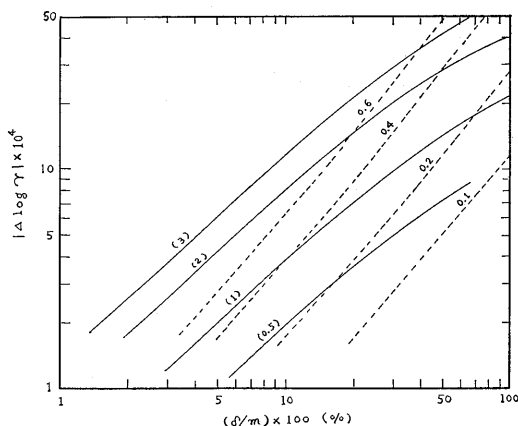


Fig. 3. Effect of activity coefficient ($I=0.8$). (Numbers in parenthesis on solid curves are values of $|\Delta m/m| \times 100$. Numbers on dotted curves are values of m .)

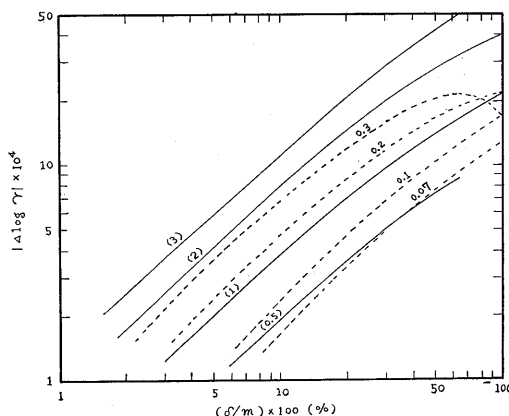


Fig. 4. Effect of activity coefficient ($I=0.5$). (Numbers on curves are similar to Fig. 3.)

activity coefficient below the desired level, the actual values of $\Delta \log \gamma$ should be so chosen as to be less than those of the curve in Fig. 3. It is seen in Fig. 3 that the allowable value of $\Delta \log \gamma$ increases as the addition rate increases, and this is due to the fact that the first term in right side of Eq. 1 increases as the addition rate increases. This relationship is shown more concretely in Fig. 1. The values of e_r in Fig. 1 were obtained by putting $|e_r|=59.15|\Delta\log\gamma|$ from the second term in the right side of Eq. 1 and calculating e_r in the unit of mV for each error of determination. For example, Fig. 1 will emerge the relationship between e_m and e_r , which should be satisfied for the errors caused by changes in the activity coefficient to remain within 1%. Such relationship, that is, the allowable value of changes in the activity coefficient varies depending upon the addition rate, is very important. A small change in the activity coefficient alone without consideration of the addition rate does not justify the conclusion

that the error of determination is small.

The problem is how much the activity coefficient varies depending upon the addition rate. The law of ionic strength⁹⁾ teaches that the activity coefficient is not dependent upon the concentration of ions in question itself, but upon the total ionic strength of the solution. On the other hand, the greater the ionic strength of the solution, the smaller the change in the ionic strength upon the addition of δ becomes. Consequently, it may be said qualitatively that the greater the ionic strength of the solution, the smaller the change in the activity coefficient caused by δ becomes to one's advantage. Moreover, there is obtained an advantage that the liquid junction potential remains nearly unchanged.

To find out what relationship should exist between the ionic strength and the amount of sodium ion to be added to confine $\Delta \log \gamma$ within the allowable limits, the assumption of MacInnes¹⁰⁾ was used in respect of activity coefficient. If the mean activity coefficient is denoted by $\gamma_{\pm}$,

$$\gamma_{\text{Na}^+} = \gamma_{\pm}^2 \text{NaCl} / \gamma_{\pm} \text{KCl} \quad (14)$$

Since there is no method known today for measuring the ionic activity coefficient, it is not possible to obtain the ionic activity coefficient without some sort of assumption. The MacInnes convention seems to be correct in the first approximation for the following reasons, and it was adopted in this paper: In their determination of the concentration of calcium ion in sea water (ionic strength, 0.7) by means of the Orion electrode, Thompson and Ross¹¹⁾ concluded that the activity coefficient of calcium ion depends only on the ionic strength in the first approximation, and the MacInnes assumption can be applied reasonably. Shatkay¹²⁾ drew the same conclusion as that of Thompson and Ross. Garrels³⁾ inferred that the MacInnes convention was applicable up to fairly high concentration.

Even when the total ionic strength of the solution is constant, it has been known that the mean activity coefficient generally varies depending upon the kind and concentration of co-existing ions, but it is not possible to express the change in the mean activity coefficient in a generalized formula. However, the fact that the potential of glass electrode responsive for sodium ion shows nearly a theoretical response to $-\log C_{\text{Na}^+}$ when the ionic strength is constant indicates that the activity coefficient is nearly constant independently of m_{Na^+} when the ionic strength is constant; namely, this fact suggests that the activity coefficient is dependent upon the ionic strength. Lanier¹⁴⁾ determined the mean activity coefficient of sodium chloride in sodium chloride-alkali earth chloride system while keeping the total ionic strength (1.0) constant. He observed that the activity coefficient of sodium chloride is nearly not affected by the concentration of sodium chloride in the sodium chloride-calcium chloride and sodium chloride-strontium chloride systems, but to some extent in the sodium chloride-magnesium chloride and sodium chloride-barium chloride systems.

For the purpose of calculation, it is necessary to express the activity coefficient of sodium ion as a function of the ionic strength (I), and the following equation whose form is similar to that of the Stokes equation¹⁵⁾ was used.

$$-\log \gamma = \frac{0.5085\sqrt{I}}{1+1.303\sqrt{I}} - \log(1+0.182I) \quad (15)$$

TABLE I. Activity coefficient of sodium ion in sodium chloride solution at 25°C

molality	0.1	0.2	0.5	1.0	2.0
$\gamma_{\pm \text{NaCl}}^{(16)}$	0.7784	0.732	0.679	0.656	0.670
$\gamma_{\pm \text{KCl}}^{(16)}$	0.769	0.719	0.651	0.606	0.576
γ_{Na^+} {Eq. 14	0.788	0.745	0.708	0.710	0.779
Eq. 15	0.784	0.744	0.709	0.711	0.777

As is shown in Table I, Eq. 15 agrees well with Eq. 14 in the intermediate concentration range. It is desirable to keep the ionic strength in the range of 0.5-1.0 where the changes in the activity coefficient of sodium ion remain small. This is explained more concretely as follows; The changes in the activity coefficient which are caused upon the addition of sodium ion in an amount of δ to the solution whose ionic strength is I can be calculated from Eqs. 15 and 16.

$$\Delta \log \gamma = |\log \gamma_{I+\delta} - \log \gamma_I| \quad (16)$$

The changes in $\Delta \log \gamma$ against the addition rate for $I=0.5$ and 0.8 are respectively shown by dotted lines in Figs. 3 and 4. It is seen from Figs. 3 and 4 that there is an upper limit for the addition rate in order to keep the error of determination below a desired level at a given ionic strength. In addition, it is desirable to make the ionic strength large and the amount of addition relatively small in order to make small the effects of the activity coefficient. For this purpose, a method is conceivable in which an organic cation which has a large ionic radius and causes less cationic errors is added as an indifferent ion to the sample solution to increase the ionic strength effectively. Garrels³⁾ set the addition rate at 2-8% in his determination of sodium ion (about 0.5m) in sea water whose ionic strength is 0.7, and what he did seems reasonable in the light of the results shown in Fig. 3.

The sensitivity of measuring instruments should be taken into consideration in examination of $\Delta \log \gamma$ values. For example, supposing the potential changes less than 0.05 mV cannot be detected, errors due to changes in the activity coefficient will not appear in the range of e_r below 0.05 mV which is equivalent to $0.05/59.15=8.4 \cdot 10^{-4}$ in the unit of $\Delta \log \gamma$ in Fig.1.

3-4. Effect of temperature

A poor temperature control causes changes in the potential gradient of glass electrode, which in turn causes the error of determination. Now, let us suppose that the potential e was measured at the apparent temperature T which was actually T' . In this instance, the potential as given by Eq. 17 is generated.

$$e = -\frac{RT'}{F} \ln \left(1 + \frac{\delta}{m} \right) \quad (17)$$

On the other hand, the apparent concentration of sodium ion, m' , is calculated from Eq. 18.

$$e = -\frac{RT}{F} \ln \left(1 + \frac{\delta}{m'} \right) \quad (18)$$

Consequently, the following equation is derived from Eqs. 17 and 18.

$$\frac{RT'}{F} \ln \left(1 + \frac{\delta}{m} \right) = \frac{RT}{F} \ln \left(1 + \frac{\delta}{m'} \right) \quad (19)$$

$$\text{or } T' \log \left(1 + \frac{\delta}{m} \right) = T \log \left(1 + \frac{\delta/m}{1 + (\Delta m/m)} \right) \quad (20)$$

The errors due to the temperature changes can be calculated from Eq. 20. It was observed that, when the temperature change is $25 \pm 0.1^\circ\text{C}$, the error of determination is less than 0.2% as long as the addition rate is less than 1%, and this does not present problems. The changes in temperature rather cause changes in the potential of inner reference electrode of glass electrode and reference electrode and also in the asymmetry potential of glass electrode, and make the errors larger for this reason.

4. Accuracy in a spike method of determining potassium ion

4-1. Potential difference generated on glass electrode

The potential e at 25°C calculated from Eq. 5 is given in Fig. 5. It is seen from Fig. 5 that e becomes larger as K becomes larger, and this is because the glass electrode

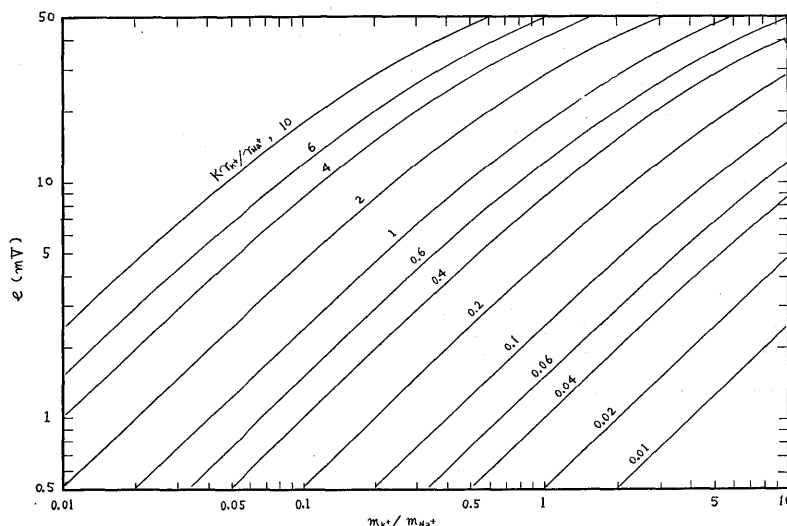


Fig. 5. Relation between e and m_{K^+}/m_{Na^+} for various values of $K\gamma_{K^+}/\gamma_{Na^+}$ (25°C).

becomes more selective in respect to potassium ion. It is desirable to have e as large as possible from the standpoint of the precision of measuring instruments and the error of determination to be described later, and to realize this it becomes necessary to make the selectivity constant large and also the m_{K^+}/m_{Na^+} ratio in the solution large. Fig. 5 will serve as a guide to estimate the magnitude of e ; it will tell what m_{K^+}/m_{Na^+} should be chosen for the electrode of a given value of K to be of any use or what K value the electrode should have at a given m_{K^+}/m_{Na^+} ratio in the solution. For example, on the basis of the error of determination to be described later, m_{K^+} in the solution should be more than twice m_{Na^+} for the electrode of $K=0.6$ when it is necessary to have e of more than 20 mV. Conversely, when the m_{K^+}/m_{Na^+} ratio is less than 0.5, the electrode with the K value of more than 3 should be used.

Next, the relationship between $e' - e$ and the addition rate (δ/m_{K^+}) which was calculated from Eq. 8 is shown in Fig. 6 assuming no changes in the activity coefficient.

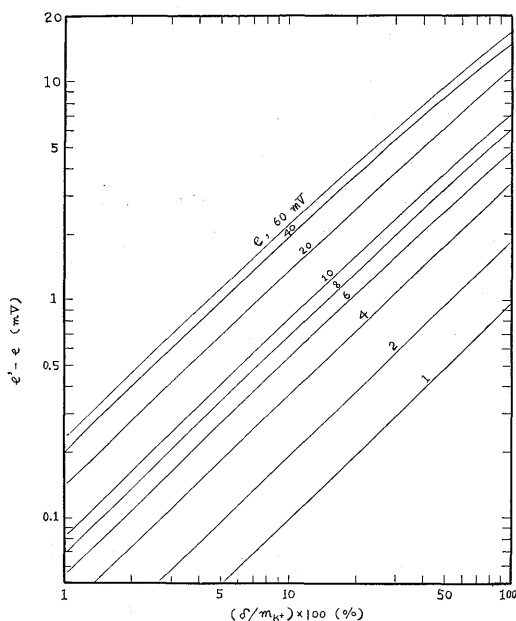


Fig. 6. Relation between $e' - e$ and δ/m_{K^+} for various values of e (25°C).

Fig. 6. Since $e' - e$ should be at least 0.05 mV from the precision of measuring instrument, and the addition rate is considered to be 10-20% in general because of the limitations imposed by the changes in the activity coefficient, it would be necessary that the value of e should be at least 4 mV.

4-2. Precision of potential difference

The infinitesimal change of m_{K^+} , dm_{K^+} , caused by infinitesimal changes of e and e' , de and de' respectively, can be given by the following equation.

$$dm_{K^+} = \left(\frac{\partial m_{K^+}}{\partial e} \right) de + \left(\frac{\partial m_{K^+}}{\partial e'} \right) de' \quad (21)$$

Now, $\partial m_{K^+}/\partial e$ and $\partial m_{K^+}/\partial e'$ are obtained from Eq. 8, and this result and Eq. 8 are put into Eq. 21 to obtain the following relationship.

$$\frac{dm_{K^+}}{m_{K^+}} = \frac{F}{RT} \cdot \left\{ \left[\frac{1}{\exp(Fe/RT) - 1} + \frac{1}{1 - \exp\{-F(e' - e)/RT\}} \right] de - \frac{1}{1 - \exp\{-F(e' - e)/RT\}} \cdot de' \right\} \quad (22)$$

By putting $de = de'$ for simplicity since the difference between e and e' is small generally and considering infinitesimal changes of e and m_{K^+} , the following equation is obtained,

$$\frac{|\Delta m_{K^+}/m_{K^+}|}{|\Delta e|} = \frac{F}{RT} \cdot \left\{ \frac{1}{\exp(Fe/RT) - 1} + \frac{2}{1 - \exp\{-F(e' - e)/RT\}} \right\} \quad (23)$$

where Δe denotes the precision of measuring instrument. As the conversion of Eq. 22 to Eq. 23 indicates, Eq. 23 represents the theoretical maximum error (When de and

From the precision of measuring instruments and the error of determination to be described later, it is advantageous to have $e' - e$ as large as possible, and for this purpose it is necessary to make e and the addition rate large from Fig. 6. However, because of the limitations imposed by changes in the activity coefficient to be described later, it is not possible to make the addition rate large unlimitedly. At any rate, it is desirable in this method to use the electrode which generates substantially large e , that is, the electrode which has a large K value in Fig. 5. Since the values of e and $e' - e$ are under some limitations to keep the error of determination below a desired level, the optimal addition rate within these limitations can be obtained from

e' have the same sign, $\Delta m_{K^+}/m_{K^+}$ can be expressed by the first term in the right side of Eq. 22 alone, and the error of determination becomes very small. They are shown by a dotted line in Fig. 7 for reference.).

The relationship between $e'-e$ and the error of determination at 25°C is shown in

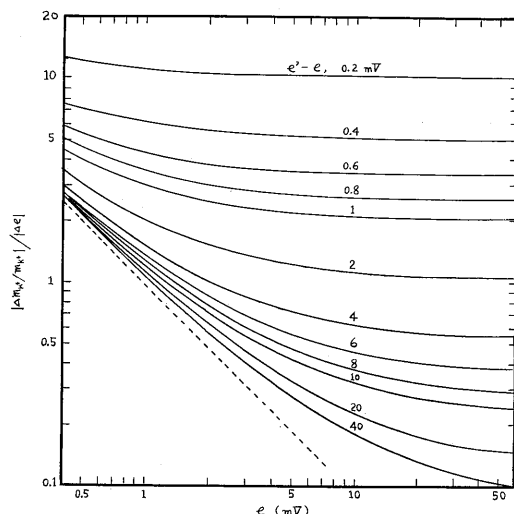


Fig. 7. Relation between $|\Delta m_{K^+}/m_{K^+}|/|\Delta e|$ and e for various values of $e'-e$ (25°C).

1 mV from Fig. 7. If $e'-e$ is about 2 mV, e should be more than 1 mV from Fig. 7. However, it is seen from Fig. 6 that the amount of addition should be made extremely large to make e 1 mV and $e'-e$ 2 mV. Now, when e is made 20 mV, the addition rate becomes 15%; that is, by using a glass electrode capable of generating e of 20 mV and a measuring instrument with the precision of ± 0.01 mV and making the addition rate at least 15%, the error of determination can be made less than 2%. In such case, the glass electrode generating e of 20 mV can be obtained from Fig. 5.

4-3. Effect of activity coefficient

Strictly speaking,

$$\frac{m_{K^+} + \delta}{m_{K^+}} = \frac{\gamma'_{Na^+} \cdot \gamma_{K^+}}{\gamma_{Na^+} \cdot \gamma'_{K^+}} \cdot \frac{\exp(Fe'/RT) - 1}{\exp(Fe/RT) - 1} \quad (24)$$

from Eqs. 6 and 7, but in the actual calculation the apparent concentration is obtained from the following equation assuming no changes in the activity coefficient.

$$\frac{m'_{K^+} + \delta}{m'_{K^+}} = \frac{\exp(Fe'/RT) - 1}{\exp(Fe/RT) - 1} \quad (25)$$

Accordingly, the following relationship is obtained from Eqs. 24 and 25.

$$\frac{\gamma'_{Na^+} \cdot \gamma_{K^+}}{\gamma_{Na^+} \cdot \gamma'_{K^+}} = \frac{m_{K^+} + \delta}{m_{K^+}} \cdot \frac{m'_{K^+}}{m'_{K^+} + \delta} = \left(1 + \frac{\delta}{m_{K^+}}\right) \cdot \frac{(m'_{K^+}/m_{K^+})}{(m'_{K^+}/m_{K^+}) + (\delta/m_{K^+})} \quad (26)$$

On the other hand, $m'_{K^+} - m_{K^+} = \Delta m_{K^+}$ leads $m'_{K^+}/m_{K^+} = 1 + (\Delta m_{K^+}/m_{K^+})$, and Eq. 26 can be converted as follows.

$$\frac{\gamma'_{Na^+} \cdot \gamma_{K^+}}{\gamma_{Na^+} \cdot \gamma'_{K^+}} = \frac{\{1 + (\delta/m_{K^+})\} \cdot \{1 + (\Delta m_{K^+}/m_{K^+})\}}{1 + (\Delta m_{K^+}/m_{K^+}) + (\delta/m_{K^+})} \quad (27)$$

Eq. 27 gives the ratio of activity coefficient necessary for obtaining the desired

Fig. 7, which indicates that it is necessary to make not only $e'-e$ but also e large to make the error of determination small. Particularly effective is $e'-e$ for minimizing the error and a selection of conditions should be made such that $e'-e$ becomes as large as possible.

It is possible to find out from Fig. 7 the amount of addition and the precision of measuring instruments to keep the error of determination below a desired level. For example, when the precision of measuring instrument is ± 0.01 mV and the error of determination is to be made less than 2%, $|\Delta m_{K^+}/m_{K^+}|/|\Delta e| = 0.02/0.01 = 2$ and $e'-e$ should be made more than

error, and it is graphically shown in Fig. 8. It is seen that the allowable value of the ratio of activity coefficient increases with increasing the addition rate, but in general changes in the ratio of activity coefficient should be small fairly strictly in order to make the error of determination small. On the other hand, the MacInnes convention¹⁰⁾ that the activity coefficient of potassium ion is equal to the mean activity coefficient of potassium chloride with the same concentration indicates that the change in the activity coefficient of potassium ion against the concentration is relatively large (see Table I). Consequently, the only way to minimize the effect of the activity coefficient would be to make the total ionic strength of the solution large and the amount of addition small as mentioned in Section 3-3.

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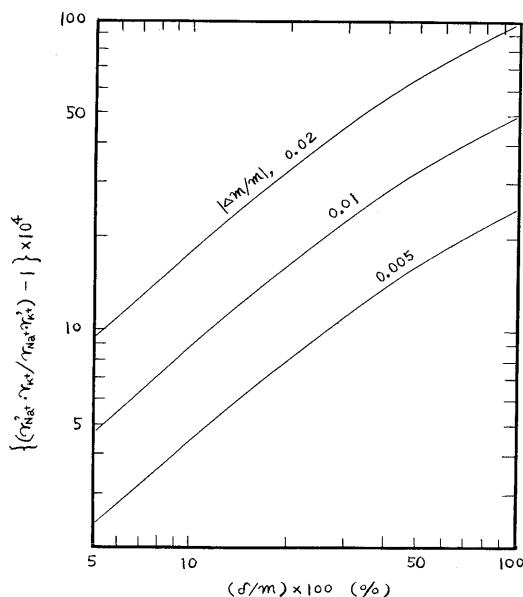


Fig. 8. Relation between $\gamma'_{Na^+} \cdot \gamma_{K^+} / \gamma_{Na^+} \cdot \gamma'_{K^+}$ and δ/m for various values of $|\Delta m/m|$.