Polarographic Determination of Sodium Chloride in Common Salt. II. Silver Oxide Method

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When magnesium salts are contained in the common salt, it gives an unsaturated diffusion current in polarogram. By experimental work on sodium chloride and magnesium chloride mixture, we found that more than 0.2% of magnesium chloride by weight showed magnitude influence as shown in Fig. I. In the common salt made by solar evaporation of sea water in Taiwan, the magnesium salts content ranges from 0.5 to 1.0% by weight and no saturated diffusion current curve used for determination of sodium chloride could be given. For this, Lee and Shen (1) gave sodium hydoxide method of the polarographic determination of sodium chloride in common salt in the first paper. That is a little excess of sodium hydroxide solution was added to the common salt solution, precipitated the magnesium as magnesium hydoxide and determined polarographically the sodium chloride and excess sodium hydroxide. and substracted the increased Na^+ from the value obtained to get the sodium chloride content. Although the result is better than that obtained by chemical analysis subatraction method, we think there are still some points need revise. First, after the magnesium hydroxide was precipitated, there left in the solution both sodium chloride and sodium hydroxide that gave different half-wave potentials and wave-heights in polarograms. Second, some sodium salt was absorbed by the colloidal precipitate of magnesium hydroxide produced by adding sodium hydroxide to common salt solution.

F. Kawamura (2) put barium chloride in common salt solution taken out the $SO4^{--}$, added silver oxide-carbonate mixture (Ag_2O:Ag_2CO_3=I:I) to precipitate Cl^- and other halogens as silver halides and Ba^{++}, Ca^{++}, Mg^{++} as carbonates or hydroxides and then after filtration, titrated volumetrically the sodium hydroxide and carbonate left in filtrate. This work was only for the artificial common salt with an error less than 0.3%. But large cost of barium salt and silver oxide-carbonate reagent, difficult to prepare the raegent, hard to filtrate the barium sulfate, and more absorption of sodium chloride and carbonate by the large quantity of pricipitates of silver chloride, magnesium, calcium and barium carbonates are troublesome.

We found occasionally when silver oxide was added instead of sodium hydroxide to common salt, silver chloride, magnesium hydroxide and excess silver oxide were precipitated and left only sodium hydroxide in the soultion equivalent to the sodium chloride originally present. As all the precipitates were easy to filtrate and wash, absorption of sodium hydroxide has eliminated to a constant minimium value. We tried to do an experimental work of the polarographic determination of sodium chloride according this process and found it gave better result than the first work.

Experimental Work.

Chemicals and stock solutions

Distilled mercury, chemical pure silver nitrate, Baker analyzed grade sodium chloride, magnesium chloride hexahydrate, potassium hydroxide and sodium hydroxide are used. 10 g/l NaCl, $MgCl_2$ and NaCl-$MgCl_2$ solutions and 7.2g/l NaOH solution with the same Na^+ equivalent to 10g/l NaCl are stock for use.

Silver oxide

Silver oxide Ag_2O, a dark brown powder is precipitated by adding solutions of silver nitrate and alkaline hydroxide together. Concentrate solutions cause rapid precipitation that give a precipitate difficult to wash free from impurities. It is prefer to use dilute solutions such as IF potassium hydroxide and 0.2 F silver nitrate. For each 7g of silver nitrate, 4g of potassium hydroxide was used, that is about 50% excess. Much brown precipitate of sliver oxide and few yellowish brown silveroxide and hydroxide mixed colloid were formed. After decanted several times to discard the colloid, filtered the brown precipitate and washed throughly. For it decomposed by heating (3), wet silver oxide was used through this work.

Analysis solutions

Treat 25cc of NaOH or NaCl-$MgCl_2$ stock solution with about 0.7g of wet silver oxide under stirring. Besure no more silver chloride would form when more silver oxide is added, washed the precipitate four times by decanted the clear upper layer, filtered and washed four times again. Collected all the decanted and washed liquor and filtrate, then diluted it to be 250 or 500cc ready for use. The concentration of sodium hydroxide in the final solution is equivalent to sodium chloride 1g or 0.5g per liter.

All experiments were carried out with Sargent-Heyrovsky polarograph Model XII, under the conditions as follows: shunt ratio 100:1 or 200:1, constant temperature, maximum bridge voltage 3.0 volts, terminal voltage of the cell=3.0×camera ring scale (0.5—0.95).

Influence of magnesium chloride

As shown in Fig. 1, polarograms of sodium chloride containing magnesium chloride gave unsaturated diffusion currents if magnesium content was more than 0.2%.

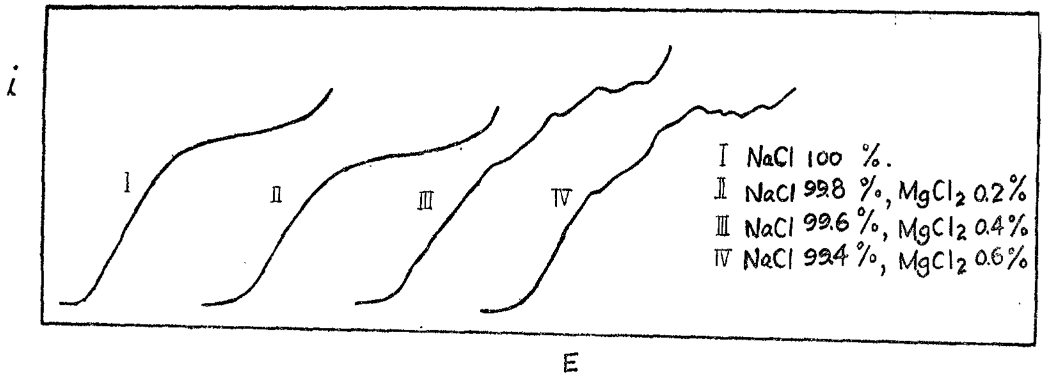


Fig. 1 Current-potentail Curve of NaCl-$MgCl_2$

Temperature effect

Silver oxide treated NaCl 99% and $MgCl_2$ 1% mixed solution gives polarographms of different wave-heights at different temperatures as shown in Table 1 and Fig. 2.

Table 1 Wave-heights of NaCl-$MgCl_2$ Solution at Different Temperatures

Temperature, °C	Wave-height, mm				
	1	2	3	mean	difference
24	95.5	95.9	95.7	95.7	
25	97.2	97.0	97.1	97.1	1.4
26	98.8	98.8	98.8	98.8	1.7
27	100.4	100.6	100.5	100.5	1.7

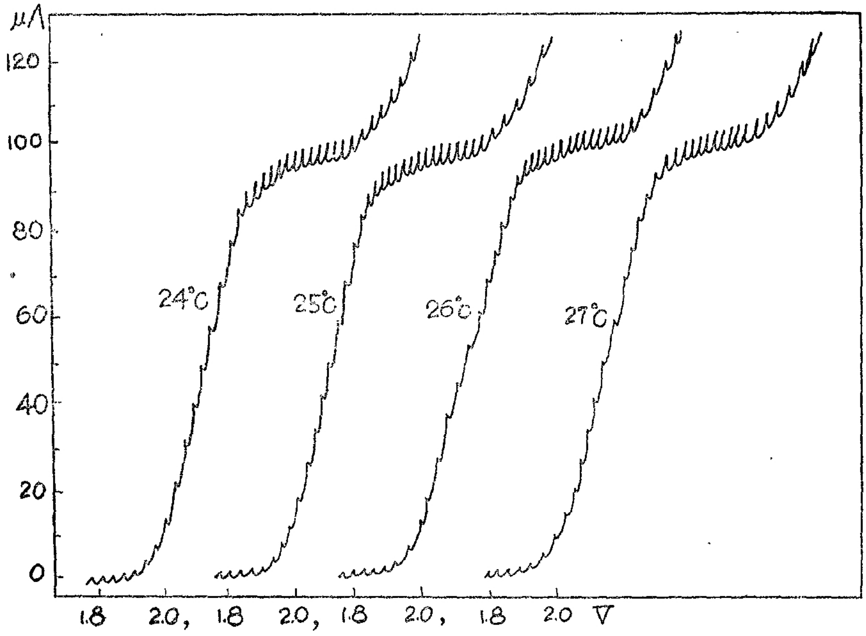


Fig. 2 Current-Potential Curve of NaCl-$MgCl_2$ Solution at Different Temperatures

As it is seen that temperature effect is pretty high, all experiments for comparison should be carried out at the same constant temperature.

Influence of anions

As the half-wave potential of a metal ion is not influenced by the concentration of a reducible substance (4), measurement of half-wave potential may help to know the influences of anions.

Althrough 1.0 g/1 NaCl and 0.72g/1 NaOH have the same amount of Na^+, but Cl^- and OH^- influence both diffusion current and reduction potential and consequently give different half-wave potentials as shown in Fig. 3, the half-wave potential of NaOH is 2.13V and that of NaCl is 2.25V.

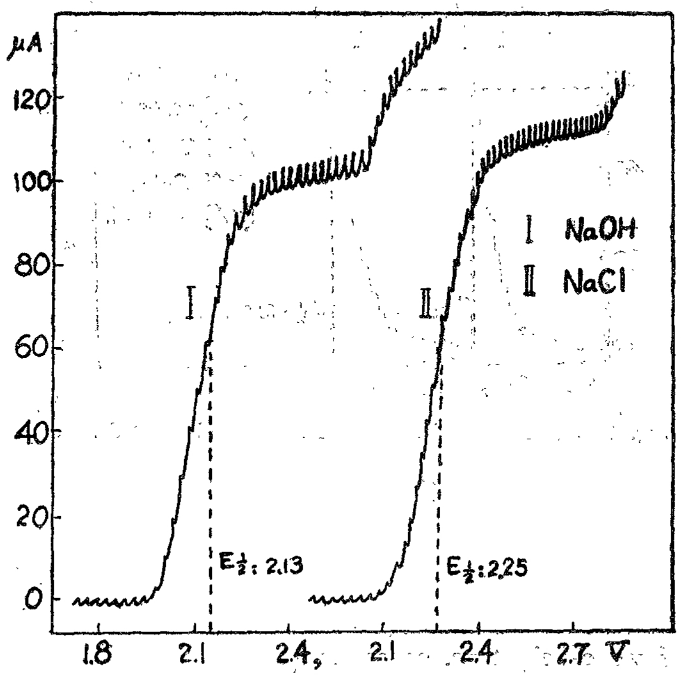


Fig. 3 Current-Potential Curve of 1.0g/1 NaCl and 0.72g/1 NaOH

If 1.0g/1 NaCl is treated with Ag_2O, it gives the same polarographm to that of 0.72g/1 NaOH, $E_{\frac{1}{2}}=2.13V$ in both cases as shown in Fig. 4.

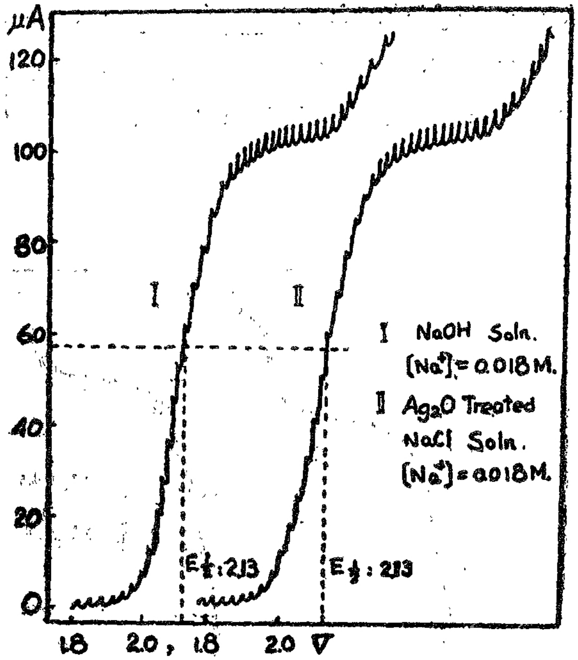


Fig. 4 Current-Potential Curve of NaOH and Treated NaCl

Correlation of wave-height vs. concentration

Taking 1.0g/1 NaCl solution as the standard let it be 100%, 99, 98, 97, 96 and 95% NaCl solutions are made. Treated with Ag_2O and analyzed polarographically. Current-potential plot is shown in Fig. 5.

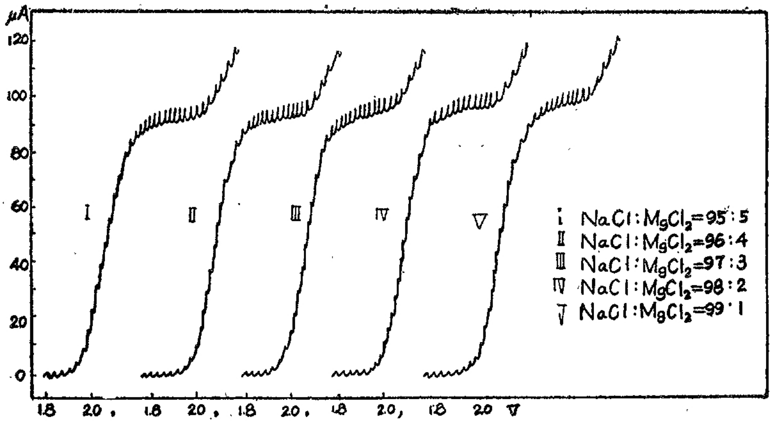
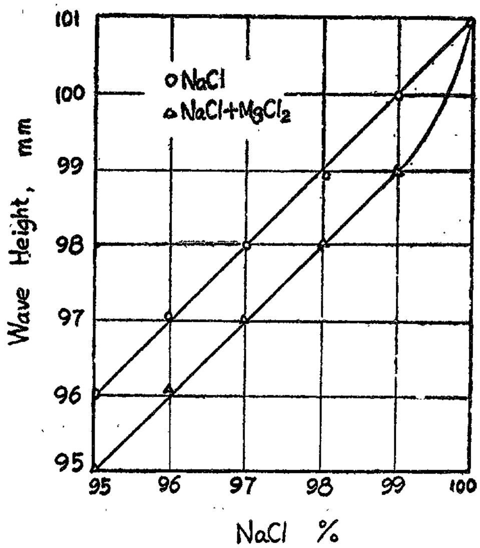


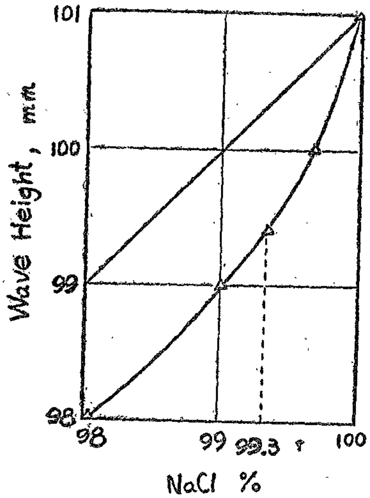
Fig. 5 Current-Potential Diagram of Treated NaCl

Correction of wave-height

Took the analysis solutions containg various amounts of magnesium with sodium chloride and treated with silver oxide. When magnesium chloride content was less than 0.7%, as its content increased, the wave-height decreased more and more. When magnesium chloride content was more than 0.7%, the decrease of wave-height kept constant as its content increased and a straight line is plotted in Fig. 6.



(a) $MgCl_2$ more than 0.7%



(b) $MgCl_2$ less than 0.7%

Fig. 6 Wave height—Concentration Diagram of $NaCl\text{-}MgCl_2$

The part outlined in heavy black lines in Fig. 6 (a) is reproduced in Fig. (b).

The wave-height of NaCl contained $MgCl_2$ is always less than that of the pure NaCl and need correction.

Analysis of common salt

Three solar evaporated sea salts made by Taiwan Salt Company, one crude and two washed, are taken for experiments. Experiments are carried out at the same conditions as cases of $NaCl\text{-}MgCl_2$ pure samples. Wave-heights of various common salts are given in Table 2.

Table 2 Wave-height of Saturated Diffusion Curve of Common Salt

Common salt	Wave-height, mm			
	1	2	3	mean
No. 1	95.9	97.0	95.6	96.17
No. 2	95.2	95.2	95.0	95.13
No. 3	90.0	90.4	89.0	89.80

For $MgCl_2$ and $MgSO_4$ contents in common salt range from 0.5 to 1.0%, the corrections should be taken from the straight line part in Fig. 6 (a), that is add 1.0mm to the wave-height and compute the NaCl content as given in Table 3.

Table 3 Corrected NaCl Content

Common salt	Wave-height, mm		NcCl %, dry base
	mean	corrected	
No. 1	96.17	97.17	96.21
No. 2	95.13	96.13	95,18
No. 3	89.80	90.80	89.90

Discussion

Silver oxide treatment

When common salt is treated by silver oxide the following reactions are taken place:

$$AgOH+Cl^- = AgCl+OH^-$$

$$Mg^{++}+2OH^- = Mg(OH)_2$$

$$AgOH = Ag+OH^-$$

Solubility products of the insoluble salts and hydroxides are as follows:

$$Ksp,\ AgOH = 1.52 \cdot 10^{-8}$$

$$Ksp,\ AgCl = 1.56 \cdot 10^{-10}$$

$$Ksp,\ Mg\ (OH)_2 = 1.4 \cdot 10^{-13}$$

1g/1 NaCl-$MgCl^2$ solution contains Cl 0.17 mole, but $MgCl_2$ content is few in comparison with sodium chloride. Neglecting the OH^- reaction with Mg^{++}, the metal ion concentrations may be computed as follows:

$$K = \frac{(OH^-)}{(Cl^-)} = \frac{(Ag^+)(OH^-)}{(Ag^+)(Cl^-)} = \frac{Ksp,\ AgOH}{Ksp,\ AgCl} = \frac{1.52 \cdot 10^{-8}}{1.56 \cdot 10^{-10}} \doteqdot 100$$

$$(OH^-) = 100\ (Cl^-), \qquad (OH^-)+(Cl^-) = 0.17$$

$$\therefore\ (Cl^-) = 0.0017, \qquad (OH^-) = 0.169$$

Therefore $(Ag^+)=\frac{Ksp,\ AgCl}{(Cl^-)}=\frac{1.56\cdot 10^{-10}}{0.0017}\doteqdot 1\times 10^{-7}$

$(Mg^{++})=\frac{Ksp,\ Mg(OH)_2}{(OH^-)^2}=\frac{1.4\cdot 10^{-13}}{0.17^2}\doteqdot 1\times 10^{-11}$

Both (Ag^+) and (Mg^{++}) are less than enough to influence the polarogram of NaOH. Silver oxide is a good reagent to eliminate magnesium as magnesium hydroxide and leaves only NaOH in solution. Therefore, to measure the wave-height of Na^+ in NaOH and compute the NaCl content is supported both by theoretical calculation and experimental work.

Correction of wave-height

As shown in Fig. 6 (a), the linear relation of wave-height vs. concentration ends at 0.7% $MgCl_2$ content. 1.0mm correction is given in case of $MgCl_2$ more than that. If $MgCl_2$ content is less than 0.7%, it should be corrected according to the differences between the two lines of Fig. 6 (b).

As shown in Fig. 5, the treated NaCl gave the same wave-height and half-wave potential as pure NaOH, we realized that there was no absorption of NaOH by AgCl precipitate at all. The only absorption happened may be that of Na^+ by the colloidal precipitate of $Mg(OH)_2$. But when the magnesium content is more than 0.7%, larger particles of precipitate set with the colloidal particles and then the more absorbed NaOH can be washed down. The washing effect is given in Table 4.

Table 4 Washing of Ag_2O Treated NaCl-$MgCl_2$ Solution

NaCl %	Wave-height, mm		
Ag_2O treated	Decanting, one time Washing, one time	Decanting, four times Washing, four times	Theoretical value
99.7	100.0	100.0	100.6
99.3	99.3	99.3	100.4
99.0	98.5	99.0	100.0
98.0	95.7	98.0	99.0
97.0	94.5	97.0	98.0
96.0	93.2	96.1	97.1
95.0	92.0	95.0	96.0

Comparison with Other methods

The silver oxide method eliminated the different effects of Cl^- and OH^- by converting all NaCl to be NaOH, reduced the absorption of Na^+ with the colloidal precipitate of $Mg(OH)_2$ by filtration and washing through to a limited value. It is not only simple and exact than the chemical substraction method, but also simple and rapid than the silver oxide-carbonate tetration method, for Ag_2O is easier to prepare in nearly pure state than $Ag_2O-Ag_2CO_3$.

As is given in Table 5, Ag_2O method gives a value about 0.7% higher than that of NaOH method, and about 1.0% lower than that of chemical analysis substraction method.

Table 5 NaCl Content* in Common Salt Determined by Various Method.

Salt	Ag_2O, corrected intersection	chemical analysis substraction	difference	NaOH intersection	difference
No.	%	%	%	%	%
1	96.12	97.18	−0.97	95.44	+0.77
2	95.18	96.27	−1.09	94.56	+0.62
3	89.90	90.98	−1.08	89.08	+0.72

*dry base

Summary

1. Silver oxide is made by the reaction of 0.2F silver nitrate with excess IF alkaline hydroxide. Brown Ag_2O precipitated with a few yellowish brown Ag_2O-AgOH colloidal particles. Separate the Ag_2O from the colloid by decantation and use it in the wet state.
2. When Ag_2O is added to the NaCl solution, AgCl and the excess Ag_2O precipitate and NaOH are left in the solution. In spite of NaCl and NaOH give different half-wave potentials, they have the same amount of Na^+. From the polarogram of NaOH, therefore, can determine quantitatively the NaCl.
3. In case of NaCl-$MgCl_2$ or common salt, when Ag_2O is added, AgCl, $Mg(OH)_2$ and excess Ag_2O precipitate and NaOH with a little amount of KOH are left in the solution. About 1.0% of NaOH is absorbed by the $Mg(OH)_2$

colloidal precipitate after washing throughly. Therefore, 1.0mm correction is added to the wave-heigh of polarogram in cases that $MgCl_2$ is more than 0.7% by weight in NaCl-$MgCl_2$ or common salt. When $MgCl_2$ content is less than 0.7%, wave-height vs. $MgCl_2$ percent diagram is available for correction.

4. The Ag_2O method eliminated the different effects of Cl^- and OH^- in NaCl and NaOH respectively and reduced the absorption of NaOH by $Mg(OH)_2$ colloidal precipitate to a limited value by washing throughly. Therefore, Ag_2O method after correction would give more exact value than chemical analysis and NaOH methods.

5. Three kinds of common salt were used for experiments at constant temperature of 25°C. We got a value about 0.7% higher than that of NaOH method given in the first paper, and about 1.0% lower than that of chemical analysis substraction method now used here.

6. Potassium is not eliminated by this method. As its cotent is usually 0.5%, it seems to be no trouble to consider potassium as sodium in common salt.

Literatures cited

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(2) Kawamura F., Chemical Times (Japan), No. 23, 373 (1960).

(3) Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 12, 441.

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食鹽中氯化鈉之極譜定量法 其二

氧化銀法

李漢英 陳世學

在食鹽經氧化銀處理後之極譜定量實驗，得到下列各點結論。

1. 硝酸銀溶液（約 0.2F）與氫氧化鹼（約 1.F）反應而生 Ag_2O 之褐色沉澱，溶液中尚浮懸有少量 $Ag_2O-AgOH$ 之黃褐色膠體。用傾瀉除去膠體，即可分得 Ag_2O 而在濕狀下使用。

2. 當 Ag_2O 加入 NaCl 溶液內，AgCl 及過剩之 Ag_2O 沉澱，而留存 NaOH 於溶液中。雖 NaCl 及 NaOH 有不同之半波電勢，惟都含有同量之 Na^+，故由 NaOH 之極譜可定量 NaCl.

3. 在 $NaOH-MgCl_2$ 系或食鹽中加入 Ag_2O，則 AgCl, $Mg(OH)_2$ 及過剩之 Ag_2O 沉澱而 NaOH 和少量之 KOH 殘留溶液中。經充分洗滌可減低 NaOH 被膠體之吸收至約 1.0%。如 $MgCl_2$ 含量超過 0.7%，加 1.0mm 於波高，即可校正，如 $MgCl_2$ 含量低於 0.7%，利用波高一濃度曲線，亦可校正。

4. 本法能消除 NaOH 法之 Cl^- 及 OH^- 共存之不同影響，並能減低 Na^+ 被膠之吸收至一極小限。校正值比較準確。

5. 臺灣製鹽廠三種食鹽在 25°C 恒溫下，供作實驗，所得值平均高 0.7% 於 NaOH 法，低 1.0% 於化學差減法。

6. 本法亦未能除鉀，因含量僅約 0.5%，將其看作鈉計算，並無防礙。