Simultaneous Determination of Sodium(I) and Potassium(I) by Adsorption Voltammetry

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In 0.05mol/dm^3 tetrabutylammonium iodide (Dimethylformamide as solvent) buffer solution (pH=4.5), the reduction peaks of Na$^+$ and K$^+$ are very close. After dibenzo-18-crown-6 is added in, K$^+$ may form complex with it. The complex can be reduced at the hanging mercury drop electrode, and gives a new reductive peak at −1.80 V which is more negative than the reductive peak of Na$^+$. The peak current of the two peaks are proportional to the concentration of Na$^+$ and K$^+$ in the range of 1.0×10^{-8} ~1.0×10^{-6} mol/dm^3 and 2.0×10^{-9} ~ 4.0×10^{-6} mol/dm^3 respectively. The detection limits are 5.0×10^{-9} mol/dm^3 and 6.0×10^{-10} mol/dm^3 separately. The proposed method has been applied to the determination of Na$^+$ and K$^+$ content in banana and its peel.

Various electrochemical studies of Na$^+$ and K$^+$ have been reported.[1,2] However, the half wave potentials of Na$^+$ and K$^+$ are very negative and close, it is difficult to obtain the polarographic wave of them in aqueous solution separately. Reports on the simultaneous polarographic analysis of them are hardly been seen. Macrocylic compounds are uncharged and contain a cavity in which a cation can be encapsulated. Though the complex thus formed are of great analytical interest,[3] there are relatively few papers dealing with such complex published on analytical journals as compared with many publications on non-analytical purpose.

Generally, the most stable complexes are formed when the crystal diameter of the cation is equal to the diameter of cavity of the macrocylic compound. Pedersen and Frensdorff[4] gave some cations and related macrocylic compounds. Dibenzo-18-crown-6 is one of such macrocylic compounds, it is a good complex former with potassium.

A certain amount of Na$^+$ and K$^+$ standard solutions, 3 cm^3 0.2% dibenzo-18-crown-6 solution, and 0.8 cm^3 distilled water were added into the cell, then diluted to 30 cm^3 with 0.05 mol/dm^3 tetrabutylammonium iodide solution.The solution was deoxygenated with nitrogen (99.9%) for 10 min. The preconcentration potential of -0.50 V (vs.Ag electrode) was applied to a fresh mercury drop. Following a preconcentration period the stirring was stopped, and after 15 s, the derivative voltammogram was recorded by applying a negative-going scan of 100 mv/s.

In 0.05 mol/dm^3 tetrabutylammonium iodide(Dimethylformamide as solvent)buffer solution, ΔE_p between Na$^+$ and K$^+$ reductive peak is only 30 mv, which is too narrow to distinguish. But after dibenzo-18-crown-6 is added in, the reduction peak of K$^+$ removes markedly to the negative direction. From Figure 1, it can be seen that the peak of K$^+$ is at -1.80 V while that of Na$^+$ is at -1.65V, ΔE_p reaches to the value of 150 mv. The wave appearing after reduction of K$^+$–dibenzo–18–crown-6 complex (it is referred to as K$^+$ complex below for short) is attributed to the reduction of background solution. It has not any influenced on the determination.

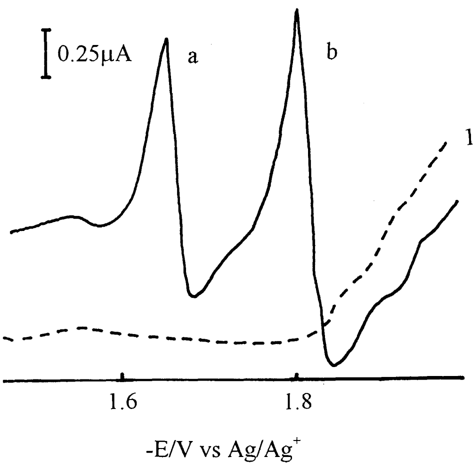

Figure 1. Derivative voltammogram.
1.background solution : 0.05 mol/dm^3 tetrabutylammonium iodide (Dimethylformamide as solvent); 0.02% dibenzo-18-crown-6.
2. background solution +
a) 5.0×10^{-7}mol/dm^3 Na$^+$; b) 2.0×10^{-7} mol/dm^3 K$^+$.
v=100mv/s; ta=60s; pH=4.5.

The voltammetric behaviour of Na$^+$ and K$^+$ complex was studied in acetone, ethylenediamine, tetrahydrofuran and tetrabutyl-ammonium iodide buffer solution. Tetrabutylammonium iodide (TBAI) was found to be the best, and optimum concentration of TBAI was 0.05 mol/dm^3 .

The content of water exists much influence on the polarographic wave. When the content of water is greater than 10%, the peak height of Na$^+$ decreased and the shape of peak became worse. Meanwhile, the peak of K$^+$ complex was stable and sensitive when the content of water varied from 1.5% to 6.0%. So 1.5~6.0% was chosen as the best experimental concentration range of water.

In 0.05 mol/dm^3 tetrabutylammonium iodide buffer solution, the difference between the two reduction peak potentials of K$^+$ and Na$^+$ is only 30 mv, which is too narrow to discern. But dibenzo–18–crown-6 contains a cavity in which K$^+$ can be well encapsulated. The complex thus formed has a more negative reductive peak potential than that of single K$^+$. By using this property, we can determine Na$^+$ and K$^+$ simultaneously. From Figure 1, we can see that when dibenzo–18–crown-6 is added in, the reductive peak of K$^+$ complex is at −1.80 V while that of

Table 1. Results of sample analysis

Sample	Content determined (μg/g)				RSD of present method	
	AAS method		present method			
	Na^+	K^+	Na^+	K^+	Na^+	K^+
Banana	1.52	3.98	1.48	4.07	2.3%	2.6%
Banana peel	0.56	3.68	0.58	3.59	2.9%	3.2%

Na^+ is at −1.65 V. The two peaks are sensitive and stable when the concentration of dibenzo-18-crown-6 is from 0.01% to 0.03%, so 0.02% is selected as the concentration of the reagent in our experiment.

The peak current of the K^+ complex increases with the increase of accumulation time, then reaches a fixed value. This indicates that the complex has the characteristic of adsorption.

The averages of temperature coefficients for the peak current of K^+ complex are as follows: 10~15 ℃, 2.0%/℃; 15~20 ℃, 1.0%/℃; 20~30 ℃, −1.2%/℃. With the increase of temperature, the temperature coefficient decreases and eventually a negative value is obtained. This is typical for a preliminary reaction of adsorbed reactants on the electrode.[5]

The effective preconcentration associated with the complex adsorption results in extremely low detection limits. The linear relationship holds between the derivative peak height of reduction of the two kinds of metals and their concentration, ranges of which are as follow: for Na^+, from 1.0×10^{-8} to 1.0×10^{-6} mol/dm^3, while for K^+, from 2.0×10^{-9} to 4.0×10^{-6} mol/dm^3. The detection limits are 5.0×10^{-9} mol/dm^3 and 6.0×10^{-10} mol/dm^3, respectively.

The experimental results showed that a 500-fold excess of Li^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and NH_4^+, a 200-fold excess of Rb^+, Cs^+ do not interfere with the determination of 1.0×10^{-7} mol/dm^3 Na^+ and K^+.

The samples of banana and its peel were pretreated and determined using the standard addition method according to the above experimental method. The results of five consecutive analyses of the samples are shown in Table 1. It can be seen that the Na^+ and K^+ contents determined by the present method are very close to those by an atomic absorption spectroscopy (AAS) method.

References

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