On the Determination of Potassium in Dilute Solution and its Application to the Analysis of Sea-water

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In order to estimate the amount of potassium in dilute solution, the dipicrylamine method has been examined and the defect that the potassium dipicrylaminate is not comepletely precipitated from its dilute solution has been eliminated by a simple method. Then, use of the method was made in the determination of the amount of potassium dissolved in sea-water.

INTRODUCTION

For the determination of potassium, there have been several well-known methods such as perchlorate, chloroplatinate, cobaltinitrite, dipicrylaminate and tetraphenylborate[1] *etc.* The dipicrylamine method was examined and then applied for the determination of potassium in sea-water.

The reasons why that method was chosen are as follows : (1) The chemical factor of the potassium in the precipitate is the smallest among the above mentioned methods, (2) the reagent is comparatively inexpensive, (3) the composition of the precipitate is always definite, (4) the solubility of the potassium salt is considerably small.

The determination of the amount of potassium in sea-water[2] seems to be simple, but detailed examination shows that conventional methods cannot be directly used and an exact value cannot be easily obtained. The principal causes are thought to be as follows : (1) In spite of the fact that the amount of potassium in sea-water is fairly small, the solubility of the potassium salt used for the determination of it cannot be generally neglected, (2) there being a great deal of other salts present, it takes a long time for the complete deposition of the precipitate or else incomplete precipitation takes place. (3) The produced potassium salt is not often recrystallized, (4) there being a large amount of sodium present, such phenomena as the coprecipitation of sodium and a change of the composition of potassium salt *etc.* take place.

The weakest point in the dipicrylamine method for the determination of potassium is found to be the incomplete precipitation of the potassium salt when the concentration of the potassium in the solution is especially small. However, it has been found that this defect can be overcome to a certain extent by the following simple procedure in which the vessel containing potassium and the reagent is shaken at certain definite intervals during its ice-cooling. It was

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found that potassium dipicrylaminate is much more rapidly precipitated by this method than by the conventional ice-cooling method.

REAGENT AND APPARATUS

8% H_{Mg} Reagent : 16 grams of dipicrylamine and 7 grams of MgO are added to 200 ml. of distilled water heated on a steam-bath for about 2 hours. After standing for 24 hours, it is filtered and stored in a bottle for use.

Injector : Their capacities are 1 ml. amd 2ml. respectively.

Spray : This is used for the dissolution of the precipitate on the filter-stick or for washing a filter-stick.

Standard Potassium Solution : 362.30 mg. of purified potassium chloride is weighed and dissolved in 100 ml. of distilled water. Then the exact amount of potassium in one gram of solution is found. One ml. of this solution contains approximately 1.9 mg. of potassium and the concentration of potassium is as much as five times that of sea-water. A definite amount of potassium was weighed using an injector.

Balance : Chemical balance and Semi-micro balance.

EXPERIMENT

(a) Procedure

A definite amount of potassium is put into the vessel of which the weight together with a glass-filter-stick has already been found. The filter-stick is kept free from dust. The solution in the vessel is diluted with distilled water until the concentration of potassium is equal to that of sea-water. Then, a definite amount of 8% H_{Mg} reagent is added and the vessel is cooled with ice for a definite time. During the ice cooling, the vessel is shaken every fifteen minutes. The precipitate is filtered with the previous glass-filter-stick and washed as follows : Once with 0.8 ml. of cold water, then three times with 0.8 ml. of the saturated solution of potassium dipicrylaminate and lastly once with 0.8 ml. of cold water. Then the precipitate attached to the filter-stick is washed down into the vessel using a micro-washing-bottle and the filter-stick is thoroughly purified by use of a spray and 0.25 ml. of acetone which is contained in an injector. In addition, the filter-stick is washed down with hot water and kept aside. The vessel is carefully warmed on a steam-bath, and the solution is vaporized until dipicrylaminate begins to deposit. Then, a definite amount of distilled water and of 4% H_{Mg} reagent are added to it and after ice-cooling for a definite time, the precipitate is filtered and washed as before. The precipitate is dried at 110°C for an hour, cooled in a desiccator and weighed.

(b) Experimental Results

The results obtained for the determination of potassium in its dilute solution by the conventional method are shown in Tables 1 and 2. As seen from these tables, the results found for definite amounts of potassium are negative when

Table 1. Determination of potassium by the conventional method (1).

K taken (mg.)	Reagent (ml.) 0.1*N*-Hca	4%-HMg	Tot. vol. (ml.)	Cooling (hrs)	HK (mg.)	K found (mg.)	Error (mg.)
1.891	2.9	—	8	2	22.30	1.827	−0.064
1.897	2.9	—	8	2	22.61	1.853	−0.044
1.896	2.9	—	8	2	22.80	1.868	−0.028
1.897	3.0	—	8	3	21.65	1.774	−0.123
1.896	3.0	—	8	3	21.76	1.783	−0.113
1.899	3.0	—	8	3	22.47	1.841	−0.058
1.898	—	3.2	8.2	3	21.90	1.794	−0.104
1.896	—	3.2	8.2	3	22.00	1.803	−0.093
1.894	—	3.2	8.2	3	21.28	1.740	−0.154
1.902	—	3.2	8.2	3	22.11	1.811	−0.091
1.895	—	3.2	8.2	3	22.59	1.850	−0.045

Table 2. Determination of potassinm by the conventional method (2).

K taken (mg.)	Reagent (ml.) 0.1*N*-Hca	4%-HMg	Tot. vol. (ml.)	Cooling (hrs)	HK (mg.)	K found (mg.)	Error (mg.)
3.894	4.3	—	14.3	2	44.85	3.685	−0.209
3.858	4.3	—	14.3	2	44.98	3.686	−0.172
3.932	4.3	—	14.3	2	45.96	3.766	−0.166
3.787	4.3	—	14.3	2	44.35	3.634	−0.153
3.788	4.3	—	14.3	2	44.20	3.622	−0.166
3.824	4.3	—	14.3	2	45.10	3.695	−0.129
3.666	—	3	13	2	44.00	3.605	−0.061
3.877	—	3	13	2	46.08	3.775	−0.102
3.877	—	4	14	2	45.06	3.692	−0.195
3.813	—	4	14	2	44.94	3.682	−0.131
3.857	—	4	14	2	44.87	3.674	−0.183

Tabli 3. Determination of potassium by the present method.

K taken (mg.)	Reagent (ml.) 0.1*N*-Hca	4%-HMg	Tot. vol. (ml.)	Cooling (hrs.)	HK (mg.)	K found (mg.)	Error (mg.)
2.079	—	3	8	2.5	25.60	2.097	+0.018
1.767	—	3	8	2.5	21.54	1.765	−0.002
1.937	—	3	8	2.5	23.67	1.940	+0.003
1.930	—	3	8	2.5	23.59	1.933	+0.003
1.868	—	3	8	2.5	22.67	1.858	−0.010
1.976	3	—	8	2.5	24.08	1.973	−0.003
1.955	3	—	8	2.5	23.94	1.962	+0.007
1.905	3	—	8	2.5	23.36	1.914	+0.009
1.915	3	—	8	2.5	23.38	1.916	+0.001
1.925	3	—	8	2.5	23.71	1.943	+0.018
1.865	3	—	8	2.5	22.74	1.861	−0.004
2.094	3	—	8	2.5	25.38	2.080	−0.014

the vessel is not shaken during the ice-cooling. Moreover it has been found that all the potassium is not precipitated by the conventional method even if the vessel is cooled for longer times, for instance, four and six hours. The results obtained by this shaking method are shown in Table 3 and show that satisfactory results are obtained by such a simple procedurs as shaking the vessel during the ice cooling. This means that the weakest point of the dipicrylamine method for the determination of potassium in its dilute solution has been overcome in the case of a potassium solution containing no other substances. However, the direct determination of potassium in an artificial sea-water by this shaking method still showed a fairly low value. This seems to be based on the increased solubility due to the salt effect. So, 8% H_{Mg} reagent was used instead of 4% H_{Mg} or 0.1*N*-H_{Ca} reagent, but now the results were found to be positive

Table 4. Determination of potassium by the reprecipitation method.

HK taken (mg.)	Acetone (ml.)	H_2O (ml.)	4%-HMg (ml.)	Tot. vol. (ml.)	Cooling (hrs.)	HK (mg.)	K found (mg.)	Error (mg.)
24.08	0.25	2	1	3	2	23.85	1.954	−0.022
23.94	〃	2	1	3	2	23.88	1.957	+0.002
23.36	〃	2	1	3	2	23.28	1.907	+0.002
23.38	〃	2	1	3	2	23.30	1.909	−0.006
23.71	〃	2	1	3	2	23.47	1.923	−0.002
22.74	〃	2	1	3	2	22.70	1.860	−0.005
25.38	〃	2	1	3	2	25.08	2.055	−0.039

Table 5. The composition of one liter of artificial sea-water.

NaCl	25.00 gram
$MaCl_2$	2.00 〃
$MgSO_4$	2.00 〃
$CaCl_2$	1.102 〃
KCl	0.725 〃
$NaHCO_3$	0.192 〃

Table 6. Determination of potassium in artificial sea-water.

K taken (mg.)	1.948	1.778	1.968	1.768	1.913	1.856	2.087	2.140
8%-Hmg (ml.)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Tot. vol. (ml.)	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Cooling (hrs)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Hk found (mg.)	23.96	22.00	24.72	21.71	23.79	22.74	25.75	21.10
K found (mg.)	1.963	1.803	2.026	1.779	1.949	1.863	2.110	2.221
Acetone (ml.)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
H_2O (ml.)	2	2	2	2	2	2	2	2
Cooling (hrs)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
HK found (mg.)	23.60	21.51	24.10	21.40	23.21	22.52	25.51	26.19
K found (mg.)	1.934	1.762	1.975	1.754	1.901	1.845	2.089	2.147
Error (mg.)	−0.014	−0.016	+0.007	−0.014	−0.012	−0.011	+0.002	+0.007

Table 7. The amount of potassium in sea-water.

Sea-water	(g.)	5.0842	5.0805	5.0864	5.0814	5.0819	5.0813	5.0738	5.0861
HK	(mg.)	24.03	24.03	24.85	24.28	—	—	—	—
H_2O	(ml.)	2	2	2	2	2	2	2	2
4%-HMg	(ml.)	1	1	1	1	1	1	1	1
Cooling	(hrs)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
HK	(mg.)	23.36	23.30	23.58	23.33	23.36	23.30	23.38	23.52
K	(mg.)	1.914	1.909	1.932	1.912	1.914	1.909	1.916	1.927
K/lkg sea-water		0.3765	0.3758	0.3799	0.3762	0.3767	0.3757	0.3776	0.3789
Error	(%)	−0.18	−0.38	+0.72	−0.25	−0.13	−0.48	+0.11	+0.47

because the reagent itself was coprecipitated with the potassium salt. Therefore the precipitate obtained had to be reprecipitated. On the other hand, it is seen from Table 4 that the reprecipitation process for a definite amount of potassium dipicrylaminate can be satisfactorily carried out. The composition of the artificial sea-water is also shown in Table 5. The results obtained with regard to the amount of potassium in the artificial sea-water by the previous procedure are shown in Table 6. It is seen from table that the amount of potassium can be determined within an error of ± 1%. Then, the amount of potassium in sea-water was determined by this method and the results obtained are shown in Table 7. As shown in the table, one kilogram of sea-water sampled at the offing of Shirahama contains 0.3772 gram of potassium.

SUMMARY

The dipicrylamine method was examined in order to determine the amount of potassium in dilute solution and the weakest point in the conventional dipicrylamine method the incomplete precipitation of potassium dipicrylaminate in its dilute solution, has been overcome by such a simple procedure as shaking the vessel during the ice-cooling and by reprecipitation. By this method, the amount of potassium in sea-water was determined and found to be 0.3772 gram per one kilogram of sea-water sampled at the offing of Shirahama.

REFERENCES

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