

CCCLIII.—*Sodium 6-Chloro-5-nitro-m-toluenesulphonate—a New Reagent for Potassium.*

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A BRIEF account (Davies, T., 1922, **121**, 786) has already been given of the interesting difference in solubility of sodium and potassium 6-chloro-5-nitro-*m*-toluenesulphonates, and the present investigation is a more detailed examination of the value of the sodium salt as a qualitative and quantitative reagent for potassium.

The solubilities (grams in 100 grams of water) of the potassium salt at 0° and 20° are 0.235 and about 0.40, respectively, which compare favourably with the solubilities of potassium perchlorate (0.705 and 1.67) and the usually accepted values of potassium chloroplatinate (0.74 and 1.12) at the same temperatures. The new reagent is a good electrolyte, being formed from a strong base and a strong acid, and can be used in cold strongly alkaline or in

dilute mineral acid solution, and is thus of wider application than the chloroplatinate (which is really a test for potassium chloride and not the potassium-ion), tartaric acid, cobaltinitrite, and picrate methods. Moreover, the ratio of the solubilities of the sodium and the magnesium to that of the potassium sulphonate (about 40 and above 170, respectively, at the ordinary temperature) is large, and potassium can accordingly be detected in solutions containing large quantities of sodium and magnesium. As is the case with the usual reagents for potassium, ammonium must be removed before the reagent is added. The reagent will detect 1 part of potassium in about 2,500 parts of water.

With regard to the quantitative side, the percentage of potassium in potassium chloride, Rochelle salt, and potassium alum has been determined by this method, and results agreeing to within 0.5 per cent. of theory are obtained. After the addition of the reagent, the aqueous solution is not evaporated almost to dryness and then treated with alcohol as in the chloroplatinate and perchlorate methods, but the reaction is carried out in aqueous solutions dilute enough to enable the potassium salt to dissolve completely at the boiling point, and the precipitate formed on cooling and standing is washed with a little water and weighed. A considerable excess of the reagent is taken, so that owing to the influence of the common ion, the solubility of the potassium salt is still more depressed. The volume of the solution is purposely taken so small that the amount of the unprecipitated salt is almost negligible.

The quantitative side, however, is capable of further development along the lines suggested on page 2981. The presence of sulphate is without prejudice to the method, the contrary being the case with chloroplatinic acid (W. A. Davis, *J. Agri. Sci.*, 1912, **5**, 56), and even with perchloric acid (Davis, T., 1915, **107**, 1679). The presence of moderate amounts of aluminium, sodium, and presumably of magnesium is not detrimental, but, on the other hand, the alkaline-earth metals must be removed.

#### EXPERIMENTAL.

The following observations amplify the descriptions already given of some of the salts of 6-chloro-5-nitro-*m*-toluenesulphonic acid and of their methods of preparation.

In the conversion of the sulphonyl chloride into the corresponding acid, boiling for three hours is sufficient to bring about complete hydrolysis of the ester intermediately formed. The hydrogen chloride produced is removed by concentration on the water-bath (or by distillation), followed by dilution with water, and by repeating this procedure several times. The sulphonic group is not hydrolysed

at all under these conditions, for the solution is completely free from sulphuric acid, even when the evaporation on the water-bath has been carried on for a period of twenty-four hours. Such a solution is converted into any desired salt by treatment with the hydroxide or carbonate of the corresponding metal. When the desired salt is only slightly soluble in cold water, it is conveniently obtained by double decomposition from an already prepared soluble salt. The potassium, ammonium, and barium salts are best obtained from the sodium salt in this way. The attempted preparation of salts of 6-chloro-5-nitro-*m*-toluenesulphonic acid by boiling the sulphonyl chloride with an aqueous solution of alkaline hydroxides resulted in considerable replacement of the nuclear chlorine atom by hydroxyl (Davies, *loc. cit.*, p. 790).

The *ammonium* salt (made by double decomposition) contains, like the sodium and potassium salts, no water of crystallisation. It usually consists of glistening laminæ, but like the potassium salt, when slowly crystallised from hot solutions, it sometimes separates in needles (Found :  $\text{H}_2\text{O} = 0.3$  per cent. 1.1763 of the anhydrous salt gave 1.2412 of the corresponding potassium salt.\* Theory requires 1.269). The *magnesium* salt is formed by treating the free sulphonic acid with excess of magnesium carbonate and concentrating the filtered solution almost to dryness. It consists of minute, compact crystals containing 2 mols. of water (Found :  $\text{H}_2\text{O} = 6.3$ .  $\text{C}_{14}\text{H}_{10}\text{O}_{10}\text{N}_2\text{Cl}_2\text{S}_2\text{Mg} \cdot 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 6.4$  per cent. 0.6185 of the anhydrous salt gave 0.7367 of potassium salt.† Theory requires 0.7515). At  $15^\circ$ , 3.5 c.c. of water rapidly dissolve 2.0 grams of the hydrated salt, hence the solubility (considerably exceeding 50 per cent.) of the salt at this temperature is probably too great for the presence of moderate amounts of magnesium to cause interference in the estimation of potassium. The magnesium salt is extremely soluble in hot water, and readily soluble in ethyl alcohol, hot and cold. Like the *aluminium* salt, it is too soluble to be conveniently obtained by double decomposition.

\* The ammonium salt was dissolved in 25 c.c. of hot water, 80 c.c. of a 15 per cent. potassium chloride solution were added, and the solution was boiled. The precipitate formed after twenty hours was washed with 15 c.c. of cold water.

† The magnesium salt was dissolved in 10 c.c. of water and treated as above with 15 per cent. potassium chloride (31 c.c.). The precipitate was washed with 10.5 c.c. of water. These and other results show that in the analysis of salts of 6-chloro-5-nitro-*m*-toluenesulphonic acid by converting them into the potassium salt, it is advisable to use as reagent excess of an almost saturated solution (at the ordinary temperature) of potassium chloride, and to wash the solution with only a small quantity of water, or better with a moderate amount of a cold saturated solution of the potassium sulphonate (see p. 2981).

Residues of the potassium salt are best reconverted into the sodium salt via the sulphonyl chloride in the following way: A mixture of the dry potassium salt (6 grams) with phosphorus pentachloride (9 grams) and phosphoryl chloride (4 grams) is heated in a boiling water-bath with exclusion of moisture, and after an hour the oily contents are poured into 200 c.c. of water. After standing for several hours, the chlorine derivatives of phosphorus are decomposed, and the residual solid sulphonyl chloride is washed with water and dried on a porous plate. The yield is almost theoretical. The product is quite pure, melts at 50°, and is converted into the sodium sulphonate in the way already described.

*Solubility of the Potassium, Ammonium, and Sodium Salts.*—Solutions saturated at definite temperatures were obtained by keeping initially supersaturated solutions in contact with the solid substance for a period of fifteen to twenty-four hours. Some of the solution was decanted or filtered from the precipitate, the solution evaporated, and the solid dried at 110°. The solubilities recorded for the temperature 12.3° are not very trustworthy, owing to the difficulty of maintaining the thermostat constant at that temperature. The temperature range investigated is from 0° to 30°; the curves, however, are probably of the same type up to 100°, since all the salts are more soluble at this temperature than at 30°. The solubility curves are of the usual simple type. The following solubility data represent grams of the salt dissolved in 100 grams of water.

*Solubility of Salts of 6-Chloro-5-nitro-*m*-toluenesulphonic Acid in Water.*

Temperature.	Potassium.	Ammonium.	Sodium.
0°	0.235	0.935	10.4
12.3	0.30	1.48	12.0
16.45	—	—	13.3
20.1	0.405	1.77	15.05
30	0.57	2.58	20.0

*Qualitative Investigation of the Reagent.*—The addition of several drops of a concentrated solution of the reagent to *N*/50 or stronger solutions of potassium chloride at once causes a precipitation of the potassium sulphonate, which separates in characteristic, voluminous scales. *N*/60 to *N*/100—Solutions of potassium chloride slowly give precipitates on keeping, and, in fact, precipitation from *N*/100-potassium chloride is extremely slow, and in warm weather does not take place. Such a solution contains 1 part of potassium in about 2,500 parts of water.

When the solution to be tested contains ammonium, it is sufficient if the ammonia is expelled by boiling sodium hydroxide solution

and the reagent added to the cold alkaline solution. The reagent can be used in cold concentrated sodium hydroxide solution (for moderately dilute solutions, see Davies, *loc. cit.*, p. 790; this vol., p. 2981), and also in the presence of dilute mineral acids. As might be expected, however, the potassium salt is moderately soluble in concentrated mineral acids.

*Quantitative Investigation of the Reagent.*—The estimation of potassium in potassium chloride, potassium sulphate, sodium potassium tartrate, and potassium alum has been undertaken in order to determine the best experimental conditions. The potassium chloride and potassium sulphate used were Kahlbaum's products ("zur Analyse mit Garantieschein") and were used without further purification. The potassium alum and Rochelle salt (Kahlbaum) were crystallised twice from water and air-dried at room temperature until no further loss of weight occurred. Some characteristic results are tabulated below.

*Estimation of Potassium in Different Salts.*

Salt.	Weight (grams).	Wt. of potassium sulphonate.		Percentage of potassium.	
		Found.	Theoretical.	Found.	Theoretical.
KCl	0.5815	2.2391	2.260	51.9	52.31
"	0.87534	3.4033	3.401	52.35	"
KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> .4H <sub>2</sub> O	1.15765	1.1942	1.189	13.87	13.83
"	"	1.1940	"	13.87	"
"	"	1.1938	"	13.87	"
KAl(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O	2.5271	1.5581	1.544	8.30	8.23
KCl	0.87534	3.3998	3.401	52.34	52.31
"	0.43767	1.7015	1.7005	52.38	"
K <sub>2</sub> SO <sub>4</sub>	0.4515	1.5184	1.502	45.3	44.9

In the cases where at least two weights of a given salt are identical, a standard solution of the salt has been prepared, and the potassium found in an aliquot part. In the other cases, the solid potassium salt has been analysed directly. The general method adopted is as follows: A hot solution of the potassium salt in 15 to 25 c.c. of water (in about the proportion of 1.5 of potassium to 100 of water) is treated with 25 to 40 c.c. (at least 30 per cent. excess of theory) of a solution of the sodium sulphonate saturated at the ordinary temperature, and gently boiled for at least five minutes until the precipitate dissolves, more water being added if necessary. After remaining for twenty-four hours at the ordinary temperature, the potassium sulphonate is collected on a Gooch crucible, well drained, slowly washed with two to three times its weight of water, and dried at 110° until its weight is constant.

The first analysis (KCl) was carried out under too dilute conditions, the salt having been dissolved in 20 c.c. of water and 40 c.c. of

about a 7 per cent. reagent solution added. The precipitate was washed with 5 c.c. of water. The second analysis of potassium chloride, those of Rochelle salt, and that of potassium alum were carried out under the more concentrated conditions already indicated. It is noticeable that all the values in the case of Rochelle salt and that in the case of potassium alum are a trifle high. These and other experiments show that when the original salt contains much sodium or other metals, it is advisable to wash, not with a small quantity of water, but with a few c.c. of a solution of a potassium sulphonate solution saturated at the ordinary temperature.

The two analyses of potassium chloride near the bottom of the table constitute an attempt to estimate potassium in the presence of a large amount of sodium hydroxide solution, by the use of which it was hoped to reduce the excess of sodium sulphonate otherwise required. In the first case, potassium chloride in 25 c.c. of water was treated with 35 c.c. of a saturated solution of the reagent, and, on cooling, 25 c.c. of a 10 per cent. sodium hydroxide solution were added and stirred with the semi-solid mass. The precipitate was collected after twenty-four hours and washed with 10 c.c. of water. The excellent result is supported by another estimation with half the quantity of potassium chloride. This interesting modification of the process has not been further pursued, as it is to be expected that the effect of the increase in the concentration of the common ion (Na), might, especially when sodium is initially present in the salt under analysis, be sometimes detrimental. The use of sodium hydroxide solution, however, would involve no pitfalls in stereotyped estimations of substances of approximately the same composition.

In the final result, potassium sulphate was dissolved in 20 c.c. of water and treated with 40 c.c. of a saturated solution of the reagent, and the precipitate after twenty-four hours was well pressed and drained with suction, but not washed with pure water at all. This was done in order to measure the effect of washing in other cases. The result, which is only a little higher than theory (0.016 on 1.502), indicates that it is not necessary to wash the precipitate with a large volume of water when potassium is initially the only metal present.

It will be noticed that the amount of precipitate is extremely large. This is because it was felt desirable in preliminary experiments to work with a moderate quantity (40 to 70 c.c.) of filtrate for "washing" purposes. With the aid of small beakers, however, there should be no difficulty in estimating the potassium (say 0.078 gram) in a salt dissolved in 5 c.c. of water, which would give

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the comparatively small precipitate of 0.579 gram. But the best way when working with relatively small quantities will be to add the weighed solid salt to the saturated solution of the reagent, dilute with the requisite volume of water (in this case 5 c.c.), boil the solution until it is clear, and then proceed as above. In this connexion, it should be remembered that the factor of the potassium salt for potassium is small, namely, 0.1347.

*Summary.*

(I) Potassium 6-chloro-5-nitro-*m*-toluenesulphonate at the ordinary temperature is less soluble than most of the ordinary potassium salts used for the detection of potassium. The sodium salt is about forty times more soluble than the potassium salt at the ordinary temperature, and in the absence of ammonium is a useful and inexpensive reagent for potassium in neutral, alkaline, or dilute mineral acid solution. By its means, 1 part of potassium in about 2,500 parts of water can be detected. The aluminium and magnesium sulphonates are very soluble.

(II) The reagent gives satisfactory results in the estimation of potassium in the presence of sodium or aluminium (and presumably of magnesium), and of sulphate. The method is at least as trustworthy as the chloroplatinate method, and in some cases may be even more convenient than the perchlorate process.

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