THE DETERMINATION OF SMALL AMOUNTS OF POTASSIUM IN AQUEOUS SOLUTIONS.[1]

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SOME years ago Morrell[2] offered a suggestion by which small quantities of potassium might be estimated. No experimental evidence was presented accompanying this suggestion, and so far as we are aware none has appeared elsewhere. Briefly, the method suggested is to separate the potassium from other bases in the form of the potassium platinic chloride, carefully free from an excess of reagents, take up in water and then add an excess of potassium iodide, when, on standing, a beautiful pink or rose color develops, which gradually deepens to a maximum intensity. By matching the intensity of the color against that which would be developed in a standard solution of known concentration, a measure of the amount of potassium present could be obtained. Qualitative tests indicated that the method could probably be so adapted as to have a great value for a class of work upon which we have been engaged for some time past, and consequently a quantitative examination of the method was undertaken. The color of the solution is due probably to the formation of a double salt of potassium iodide and platinic iodide or chloride, and is but indirectly a method for the detection or estimation of potassium, the same reaction being well known as a delicate one for the detection of small amounts of platinum in solution.

To test the accuracy with which the colors may be compared, a series of solutions of potassium platinic chloride was prepared containing the amounts indicated in the table, expressed in parts of potassium (K) in one million of solution.

TABLE I.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
Calculated	0.16	0.31	0.62	0.94	1.40	2.03	2.81
Found	0.17	0.33	0.64	0.94	1.40	2.01	2.81

A portion of (*g*) diluted four times was used as a standard for comparison. An inspection of the figures indicates that the method is capable of a high degree of accuracy, the greatest divergence between the calculated and found amounts in this series

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[1] Published by permission of the Secretary of Agriculture.

[2] This Journal, 2, 145 (1880).

being but one part in 50,000,000 parts of solution, although a percentage error slightly greater than 6 per cent. is involved. Nevertheless, considering the magnitude of the quantities involved, the result must be considered quite satisfactory.

A second series of solutions was prepared, the results of which are given in Table II in terms of potassium in 1,000,000 parts of solution.

TABLE II.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
Calculated	0.175	0.35	0.70	1.05	1.57	2.28	3.15
Found	0.15	0.295	0.65	1.05	1.55	2.28	3.12

In this series, rather larger amounts of potassium iodide and of acid were used than in the first series, the results of which are given in Table I. The agreement between calculated and found results is not quite so happy in this case as in that recorded in Table I. The comparisons were made with much more difficulty, for the reason that the more dilute solutions showed a decided yellow tinge as compared with those of higher concentration. The cause for this will be discussed presently. Nevertheless it was decided to take solution *d* as the standard and make the determinations under the very adverse conditions obtaining. The results, while not as satisfactory as those presented in Table I, yet showed that the method could be used to give fairly satisfactory ideas as to the amounts of potassium in very dilute solutions, providing the separation of the potassium could be effected from other bases which form slightly soluble double chlorides with platinum. A seaching trial was then given the method, using solutions of potassium of known and of unknown strength, solutions of pure salt, and those containing the salts of other bases as well. Certain details of manipulation were found advisable and in some cases even essential to the successful use of the method, so that we feel justified in stating them here at some length.

If the solution under examination contain ammonium salts or organic matter, these must be removed, as the ammonia would precipitate a slightly soluble double chloride with platinic chloride, and the organic matter would color the solution and thus interfere with the reading. To effect their removal, the solution is evaporated with a few drops of sulphuric acid; enough to unite with all the bases presented. When dry, the residue is heated over a naked flame, at first gently, then strongly. After cooling, a few drops of hydrochloric acid and of platinic chloride solution are added. The amount of these will depend upon the amount of residue. The platinum must, of course, be added in excess. This may be judged fairly well by observing whether the solution is yellow after any precipitate has settled out. The platinic chloride solution is run around over that portion of the dish containing the residue, a few drops of water, free from ammonia, being added if necessary. It is again evaporated to dryness on a water- or steam-bath. All operations after the ignition with sulphuric acid must be so conducted that no ammonia has access to the solutions. In the absence of ammonium salts and organic matter, the use of sulphuric acid may be dispensed with, the platinic chloride and a very small amount of hydrochloric acid being added to the original solution, one evaporation sufficing. When dry, or in the condition of a very stiff paste (but in the small quantities usually involved, the residue will be a thin layer over the bottom of the dish and may be carried to dryness) the dish is cooled, and the potassium platinic chloride washed, as described below. An excess of platinic chloride must have been used to throw down all the potassium, and as the color to be finally read is a measure of the platinum then present, it is obvious that all the forms of platinum other than potassium platinic chloride must be removed. To effect this with the solution of as little as possible of the precipitated potassium platinic chloride, we have used in our earlier work alcohol nearly saturated with this salt. Such a solution will only slowly dissolve the precipitate, and should a little of the alcohol evaporate, there will be no separation of potassium platinic chloride. We have washed and filtered through asbestos, resting on Witt or Hirsch plates fitted into carbon filters, using gentle suction. By this means the washing is done rapidly and there is a minimum evaporation of the alcohol containing potassium platinic chloride, if the suction be shut off as soon as the alcohol has passed through. The final washing is with ordinary strong alcohol, running through four or five small portions to remove the alcohol saturated with potassium platinic chloride. There is apparently a balancing of errors here, so that we have looked into this point very carefully, and have found that, while potassium platinic chloride has an easily measurable solubility in alcohol if the two are left in contact sufficiently long, yet this solubility is so small and takes place so slowly that in repeated experiments the alcohol used in washing the precipitate, as we have described above, would have no appreciable effect on the potassium platinic chloride in the precipitate. We have, therefore, abandoned the alcoholic solution of potassium platinic chloride, and wash the precipitate at once with six or eight small portions of 95 per cent. alcohol, being careful to remove each portion as completely as possible before the next one is added.

Should the alcohol have crept up the sides of the dish or funnel, carrying with it platinic chloride, any deposit of the latter must be carefully removed. After the washing is completed, the potassium platinic chloride is dissolved and washed through the asbestos with hot water into a flask, allowed to cool, a drop of concentrated hydrochloric acid is added, and then a solution containing potassium iodide until there is present a decided excess of this reagent. To secure the desirable tint of red, the color should be developed in a strong solution, and any necessary dilution be made some time (about four or more hours) later. It is, therefore, better not to dilute further than necessary in washing the potassium platinic chloride out of the filter before adding the hydrochloric acid and the potassium iodide.

In order to compare the test solutions with a standard, the procedure adopted is to place the solution under examination in a glass cylinder with a bottom ground flat and polished, such as the well-known apparatus used for determining ammonia by the Nessler method. A second cylinder with precisely the same dimensions as the first, but made with a side arm at the bottom, contains the standard solution. Both cylinders are clamped into position parallel with each other, within a box or camera[1] fitted with mirrors, so that a beam of light can be thrown through the cylinders from above and the images of their cross-sections be seen on a lower mirror arranged at a convenient angle. The bottoms of the cylinders rest upon a shelf with orifices so arranged that no light from the upper mirror falls upon the lower mirror other than that which passes through the columns of liquid contained in the cylinders. By means of the side arm and rubber tubing, the cylinder containing the standard solution

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[1] A convenient form of instrument for this purpose is that described by Whitson, Bull. No. 85, Wis. Agr. Expt. Station.

is connected with a movable reservoir outside the camera which can be raised or lowered at will, thus regulating the depth of the standard solution within the cylinder. This depth of the standard solution is adjusted until the intensity of color of the two images is the same. The cylinder containing the standard solution is fitted with a scale, for which purpose a strip of cross-section paper pasted along the side answers very well, and is then calibrated on the assumption that when the images given in the camera by two solutions contained in identical cylinders are the same, the concentrations of the two solutions are inversely proportional to the height of the two columns of liquid. This assumption is not free from objections on theoretical grounds, but has been found entirely justifiable in the case here considered, as the result of long and repeated series of experiments. It carries with it as a necessary consequence the further assumption that the color produced by the solution in a standard cylinder is dependent only upon the amount of coloring-matter present and not upon the amount of water, a point of importance, since it enables one to avoid having always to dilute the test solution to mark in the cylinder, which procedure might sometimes be undesirable, as the following pages will show.

The substance which causes the red color in these solutions has not been determined. An inspection of the literature describing the double halides of platinum and potassium failed to give any positive information, and we have not felt justified at the present time in extending our investigation so as to definitely decide this question. In order to obtain some idea as to the proportions of the reagents necessary to the use of the method, a series of experiments was made.

For this purpose ten solutions were prepared, each containing the same amount of potassium platinic chloride, this salt being used instead of platinic chloride, since it is possible to weigh the desired amount of platinum more accurately with the former than with the latter salt. And since there was no purpose of studying the relation of the solution to solid phases, they were in all cases, after the addition of potassium iodide, brought to a volume of about 50 cc., enough to have no solid phase present at the beginning of the experiments. In each solution there was brought the amounts of potassium iodide indicated in the table. The ratios are approximate only.

TABLE III.

Weight of K_2PtCl_6 taken. mg.	Weight of KI required to form K_2PtI_6. mg.	Weight of KI used. mg.	Ratio of KI used to that required to form K_2PtI_6.	Remarks.
a···3.105	6.26	1.093	0.2 : 1	Pink, soon darkened, the pink color disappeared and a black residue separated out.
b···3.105	6.26	2.395	0.33 : 1	
c···3.105	6.26	3.975	0.66 : 1	
d···3.105	6.26	7.95	1.25 : 1	Pink; turned dark after a time; black residue.
e···3.105	6.26	15.9	2.5 : 1	Pink; shining metallic film.
f···3.105	6.26	31.8	5 : 1	Pink.
g···3.105	6.26	47.7	7.5 : 1	"
h···3.105	6.26	63.6	10 : 1	"
i···3.105	6.26	79.5	12.5 : 1	"
k···3.105	6.26	95.4	15 : 1	"

Solutions (*e*) to (*k*) inclusive, were of a satisfactory pink or red color, which apparently remained permanent for seven days. A very careful examination with starch paste at the end of that time yielded a faint reaction for iodine in some of the solutions, and the experiments were then abandoned. The results showed that it would be desirable to use about five times the amount of potassium iodide required by calculation to form the salt of the formula K_2PtI_6, but that no obvious advantage was produced by having a larger excess present.

It early developed in the work that the color of the solution did not reach a maximum until some hours after the reagents were brought together, and that the speed of the reaction was greatly augmented by the presence of a little free acid.[1] Therefore, a series of solutions were prepared from one containing about two parts per million of potassium to which the two drops of the acids indicated were added, the acids being taken from the ordinary reagent bottles of the laboratory shelf and marked "concentrated." Readings were made in the times indicated, a solution whose strength was known approximately (but not accurately), and in which the rose color had been developed twenty-four hours previously being used as the standard.

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[1] It is obvious that the amount of free acid permissible is very small, otherwise iodine would be liberated.

TABLE IV.

Acid used.	After 1 hour.	After 1½ hours.	After 4½ hours.	After 22 hours.
No acid	Trace	Trace	Lost	....
	Trace	Trace	0.20	0.33
Hydrochloric	1.33	1.53	1.93	1.93
	1.33	1.56	1.86	1.93
Acetic	0.46	1.13	1.83	1.86
	0.53	1.13	1.80	1.86
Nitric	1.33	1.53	1.73	1.86
	1.26	1.53	1.80	1.86
Sulphuric	1.33	1.56	1.86	1.93
	1.33	1.60	1.93	2.00

The results of these experiments, with many others which it is not worth while recording here, have led us to the procedure of adding one drop of strong hydrochloric acid to the solution before adding potassium iodide and then waiting at least four hours for a full development of the color before reading in the colorimeter. It has, moreover, been found desirable to make all dilutions, even of strongly colored solutions, at least one hour before readings are taken. The pink color can be brought to its maximum intensity within a comparatively few minutes, by warming the solution, and this procedure we occasionally follow rather than the one just advised. But unless great care has been taken to eliminate all traces of alcohol before dissolving the precipitate from the alcohol, warming the solution is apt to produce a yellowish or brownish tinge in the pink color, rendering its comparison with the standard much more difficult, if not impossible.

To test the efficiency of the method when other bases than potassium are present, a series of experiments were made, the results of which are given in the following table. Since becoming more expert in handling the method, we generally obtain more satisfactory results than these, but we give them here as actually obtained when working out the method, as indicating the probable order of accuracy to be expected by one having no previous experience with the method. Except as otherwise indicated, all results are expressed in this paper as parts per million of solution.

TABLE V.

Calculated.	Found.	Remarks.
50	52.7	50 parts Na, 50 parts Mg, and 50 parts Ca per 1,000,000 parts solution, also present.
	48.0	
	48.0	
	53.5	
	52.7	

20	19.8	20 parts Na, 20 parts Mg, and 20 parts Ca per 1,000,000 parts solution, also present.
	19.4	
	20.2	
	21.0	
	19.4	
5	6.4	5 parts Na, 5 parts Mg, and 5 parts Ca per 1,000,000 parts solution, also present.
	6.4	
	6.9	
	6.0	
20	20.2	No other base present.
	20.1	
	20.1	
	20.0	
	12.2	Aqueous extract of a soil.
	11.9	
	11.2	" " " "
	11.5	
	30.6	" " " "
	30.2	
	20.3	" " " "
	24.3	
	9.7	" " " "
	9.3	
	12.7	" " " "
	13.8	
	58.0	" " " "
	61.0	
	13.0	" " " "
	14.5	

To test the method still further, the three solutions cited above and containing sodium, magnesium and calcium, as well as potassium, were further examined, comparisons being made with solutions containing 2 parts and 3 parts per million of potassium, respectively, and the potassium being estimated gravimetrically as well, according to the well-known method of weighing the precipitated potassium platinic chloride, large volumes of the solutions being taken for this purpose. The results have been tabulated as follows:

TABLE VI.

Calculated.	Gravimetric.	Standard 2 parts per million.	Standard 3 parts per million.
5	4.7	5.2	5.3
	4.2	5.2	5.3
20	..	20.5	20.4
	22.5	20.5	20.4
50	50.7	49.0	48.8
	...	48.5	48.8

These results show that the method can be regarded as fairly satisfactory, even when relatively large proportions of other bases are present. The method has been used successfully with solutions containing originally as much as 400 parts per million of potassium, by properly diluting. But we do not advise its application to solutions containing more than 50 parts per million of this base, at most, unless the volume at command is so small as to prevent obtaining a sufficiently large precipitate to weigh satisfactorily. The method seems to be most satisfactory when applied to solutions containing from 1 to 10 parts per million of the base, and on the whole the most satisfactory concentration for the standard we have found to be 2 parts per million. For solutions containing less than 2 parts per million, the method has been found quite satisfactory, if care be exercised. The weak point of the method is obviously the handling and washing of the precipitate of potassium platinic chloride, and the smaller this is, the greater the difficulty becomes, and in consequence the greater the care which must be exercised.

Attention has been called above to the fact that the solutions to which the potassium iodide had been added were sometimes brownish or yellowish, thus rendering their comparison with others impossible or at least unsatisfactory. The cause of this escaped us for some time. But the fact that the pink color is not produced when potassium iodide is added to an alcoholic solution of platinic chloride, led Mr. J. F. Breazeale, of this laboratory, to suspect that small quantities of alcohol left in the filter, when washing the potassium platinic chloride free from other salts, and subsequently brought into the solution on the addition of hot water, might be responsible for the trouble. Experiments have amply verified this view. The addition of small amounts of alcohol to aqueous solutions in which the pink color had already been developed, invariably turned them yellow. This change to yellow was found to take place more rapidly in the sunlight. If the solution containing the platinum salt and to which the potassium iodide has been added together with a little alcohol, be heated, the pink color first appears, develops very rapidly, but always with a yellowish or brownish tinge, and after a few minutes turns to a clear yellow. The presence of a free acid retards the development of the yellow color, and if this color be desired in the first place, acid should preferably not be added. The yellow color is not so intense as the pink we have been describing, but much stronger than the yellow obtained from an equivalent amount of platinum combined as platinic chloride. We have, therefore, examined it with a view to its application for the quantitative estimation of platinum and indirectly of potassium.

A series of solutions containing known amounts of potassium was prepared. Mr. Breazeale and Mr. J. G. Smith, of this laboratory, were requested to read them independently against standards prepared by themselves, developing first the pink color and then subsequently developing the yellow color in the identical solutions which had just been read, and then re-reading. The results obtained follow under the headings B and S.

TABLE VII.

	Found by B.		Found by S.	
Calculated.	Pink.	Yellow.	Pink.	Yellow.
0.75	0.80	0.84	0.70	0.80
1.25	1.20	1.26	1.10	1.30
1.25	1.20	1.34	1.30	1.30
2.50	2.48	2.62	2.40	2.40
2.50	2.48	2.52	2.40	2.40
3.75	4.44	3.40	4.00	3.80
5.00	...	5.30	...	...
5.00	...	5.10	...	...
10.00	...	10.00	...	...
10.00	..	10.00	...	...

A series of water extracts of soils was then prepared, in which other bases than potassium would also be present, and they were compared by means of both the pink and the yellow color methods. The results follow:

TABLE VIII.

Pink.	Yellow.
2.4	2.8
12.5	13.5
4.2	4.4
17.7	17.1
5.7	5.4
18.8	18.9
23.9	26.2
4.4	4.7

From the results it would appear that the yellowish color can be used as well as the pink over the range of concentrations indicated in these tables. The yellow color is probably somewhat easier to "match" than the pink, and its use is advised when the higher concentrations are concerned. It is also of considerable advantage in that it affords a ready check upon the determination by the pink color, a matter of importance when such small amounts of unknown solutions are available as to preclude duplicate determinations. The yellow color is not so deep or strong, however, as the pink, and for this reason the latter is much more advantageous than the former, when high dilutions are concerned.

From what has been presented in this paper, it is evident that we have here a very sensitive method, susceptible of a high degree of accuracy, for determining quantitatively minute quantities of potassium. No unusual apparatus or skill is required for its manipulation. But it will only yield satisfactory results when care is exercised, and especially in the handling and washing of the small precipitate of potassium platinic chloride. The limit of dilution to which the method is applicable is probably much higher than the figures given here would indicate, but we have not attempted to determine this limit, and are not prepared to make a more definite statement concerning it.

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THE ESTIMATION OF TITANIUM.

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OF THE many elements which present themselves for determination to the metallurgical chemist of to-day, there are a select few which have won for themselves a reputation based upon the tediousness or the difficulty of the preliminary separation from other constituents which may be present. In this class of unenviable reputation we may place the element titanium for, although its determination presents no difficulties to the experienced chemist with time at his disposal, his less fortunate brother, at the same task in the rush of a works laboratory, is apt to find that either speed or accuracy must be sacrificed in answer to the demands made on him.

For three-quarters of a century the estimation of this element