

Because of rotation around the bonds the relative positions of the $-\text{COOC}_2\text{H}_5$ groups in the molecule do not have large effects upon the moment.

The absence of marked difference in moment between the long and the short-chain esters is regarded as indicating that the long-chain molecules have extended structures, which do not bend appreciably in small external electric fields.

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THE RAPID COLORIMETRIC ESTIMATION OF POTASSIUM

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Some months ago the writer published a paper¹ setting forth the merits and demerits of the picric acid test for potassium from a qualitative point of view. Further experiments have since demonstrated that this reaction may be utilized for the colorimetric estimation of small amounts of potassium by separating the precipitated potassium picrate, dissolving it in water, and using the intensely-colored yellow solution thus obtained for the determination of the element.

Factors Influencing the Quantitative Precipitation of Potassium as Picrate by Alcoholic Solutions of Picric Acid.—In addition to the marked influence of the ratio of the volume of the reagent to that of the potassium solution on the sensitivity of the reaction, noted in the previous paper, it was found that the temperature during precipitation was of importance from the quantitative standpoint. In the accompanying graph are shown the results of several experiments (Fig. 1) in which the amount of potassium picrate precipitated at various room temperatures is compared colorimetrically with that precipitated at 20°. This effect is apparently due to the rapid increase in the solubility of the precipitate with rise in temperature. It is evident that for comparative quantitative results in any colorimetric method involving this reaction the potassium, in a single series of experiments where standards and samples are prepared for matching, they must be precipitated under like temperature conditions or, better, a definite temperature must be established for all precipitations. It is apparent from the graph that for the sake of greater completeness of precipitation this temperature should be nearer the lower limits of room temperature rather than the higher. A temperature of 20° was found to be satisfactory. Temperatures much below this, while resulting in the more complete precipitation of the potassium, are not satisfactory due to the precipitation of the picric acid from the reagent saturated at room temperature and to

¹ Caley, *THIS JOURNAL*, **52**, 953 (1930).

increased interference from sodium. The influence of agitation and time of standing on completeness of precipitation were also studied. It was found that a forty-five-minute period of standing with occasional stirring was adequate in all cases providing the solution was stirred sufficiently at the beginning to start the separation of the precipitate when dealing with amounts of potassium near the lower limit of precipitation.

Experiments on Methods of Collecting and Washing the Precipitated Potassium Picrate.—The nature of the reagent introduced certain difficulties in the way of sharply separating the precipitate from the excess of reagent.

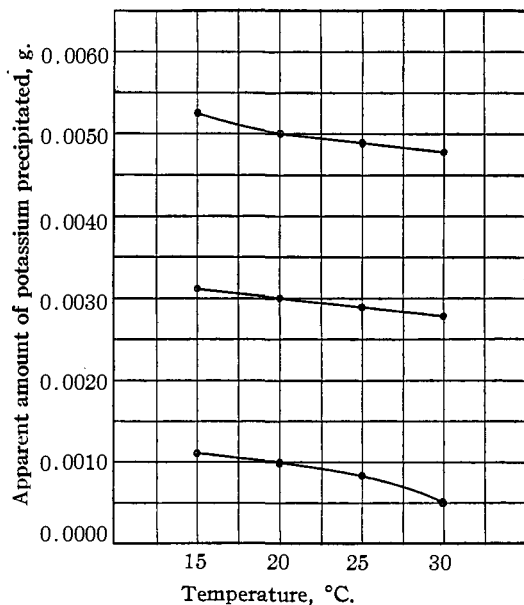


Fig. 1.—Showing the effect of temperature on completeness of precipitation in the reaction between potassium chloride solutions and saturated alcoholic solutions of picric acid.

Due to the direct dyeing action of picric acid, filtering mediums containing minute pores, such as filter paper and even asbestos, were found to be unsuitable. A number of experiments demonstrated that it was extremely difficult completely to wash out the picric acid from such filters, with any liquids suitable for this purpose, without applying an excessive number of washings, and yet on the subsequent dissolution of the precipitate in water variable amounts of the remaining picric acid went into solution, thus introducing sensible errors in the colorimetric comparison. It was found, however, that the use of a medium-porosity, sintered-glass filtering funnel or crucible permitted the sharp separation of the precipitate and excess reagent with ease. The picric acid is apparently not adsorbed in such glass filters and is readily removed with a few washings. Several washing mediums were tried, such as 95% alcohol, 95% alcohol saturated with potassium picrate and ethyl ether. It was found that the latter was the most satisfactory of these due to the ready solubility of picric acid and the high insolubility of potassium picrate in this liquid.

Accuracy Obtainable in the Colorimetric Comparison of Potassium Picrate Solutions.—In order to ascertain the observational error inherent

in the way of sharply separating the precipitate from the excess of reagent. Due to the direct dyeing action of picric acid, filtering mediums containing minute pores, such as filter paper and even asbestos, were found to be unsuitable. A number of experiments demonstrated that it was extremely difficult completely to wash out the picric acid from such filters, with any liquids suitable for this purpose, without applying an excessive number of washings, and yet on the subsequent dissolution of the precipitate in water variable amounts of the remaining picric acid went into solution, thus introducing sensible errors in the colorimetric comparison.

in matching solutions of potassium picrate, experiments were performed in which the same solution was divided and comparison made between the two parts in a plunger type colorimeter. The following table gives the results obtained with solutions of different concentration and shows the average values of the pairs of colorimeter readings after two, five and ten successive observations.

TABLE I
OBSERVATIONAL ERRORS IN THE COMPARISON OF IDENTICAL POTASSIUM PICRATE SOLUTIONS

Concn. of potassium, g./cc.	Averages of readings after two comparisons, mm.		Averages of readings after five comparisons, mm.		Averages of readings after ten comparisons, mm.	
		Errors, %		Errors, %		Errors, %
0.00002	L 29.0		L 28.2		L 28.9	
	R 28.2	2.8	R 27.9	1.1	R 28.6	1.0
.00010	L 10.7		L 12.1		L 11.1	
	R 10.6	0.9	R 12.0	0.8	R 11.1	0.0
.00020	L 11.1		L 9.9		L 9.4	
	R 10.4	6.3	R 9.7	2.0	R 9.5	1.1

From the above results it is evident that solutions of the concentrations shown may be balanced colorimetrically with an error of not more than about 1% providing at least ten separate observations are made and the results of these averaged. Solutions of potassium picrate much outside the range of concentration shown in the above table cannot be matched with this degree of accuracy. For amounts of potassium from one to ten milligrams the above experiments also indicated that a solution of the corresponding amounts of potassium picrate in fifty cubic centimeters of water would yield solutions of proper concentration for accurate matching. The best conditions for matching such solutions appear to be reached when depths of solution are used that show a strong straw color and when a strong white light is used as the source of illumination.

Recommended Procedure.—On the basis of the experiments outlined above the following method was evolved.

Procedure

Evaporate the solution, containing the potassium as the chloride, to dryness on the steam-bath in a 25-cc. beaker. Dissolve the residue in 1.00 cc. of water and add, with stirring, 7.5 cc. of a saturated solution of pure picric acid in 95% alcohol. Place the beaker in a dish containing water at 20° to maintain a definite temperature during precipitation and, if necessary, stir the solution until a precipitate starts to form. Let the mixture stand for forty to forty-five minutes and stir at five-minute intervals in order to promote complete precipitation. Filter off the separated potassium picrate in a medium-porosity, sintered-glass filtering funnel

or crucible and, after the excess reagent has passed through the filter, transfer the small portion of precipitate remaining in the beaker to the filter by washing out with small portions of ether. Wash the precipitate with successive 1-2 cc. portions of ether until the washings are colorless and no trace of yellow color due to picric acid can be seen in the sintered glass disk or on any part of the filtering crucible or funnel. Usually five to ten washings will be required. Free the precipitate from ether by continuing the suction for about one-half minute after completing the washing and then dissolve the precipitate in successive small portions of water, catching the resulting solution in a 50-cc. volumetric flask. After mixing, compare the yellow solution with a standard potassium picrate solution representing approximately the same amount of potassium. The standards are prepared from a potassium chloride solution of known value by means of the above procedure. A convenient solution for this purpose is one containing 1.907 g. of pure potassium chloride per liter, 1.0 cc. of which represents 0.0010 g. of potassium.

Results Obtained with Known Amounts of Pure Potassium Chloride.—The comparison of samples and standards prepared by the above procedure was found to give satisfactory results in all cases when the amount of potassium present, in the sample and standard compared, was identical or nearly so, as the results in Table II show, while on comparing samples with standards containing different amounts of potassium the results were

TABLE II
THE DETERMINATION OF POTASSIUM IN VARIOUS SAMPLES USING STANDARDS
REPRESENTING THE SAME AMOUNTS OF POTASSIUM

Potassium present in Standards, g.	Samples, g.	Colorimeter readings (each value the mean of ten observations)		Potassium found, g.	Differences, g.
		Standards, mm.	Samples, mm.		
0.0010	0.0010	27.9	29.6	0.0009	-0.0001
	.0010	29.7	31.0	.0010	.0000
	.0010	27.0	25.5	.0011	+ .0001
	.0010	29.8	27.6	.0011	+ .0001
	.0010	31.7	31.4	.0010	.0000
.0015	.0015	26.0	25.6	.0015	.0000
	.0015	26.2	25.8	.0015	.0000
.0020	.0020	17.9	17.7	.0020	.0000
	.0020	20.1	19.8	.0020	.0000
.0030	.0030	27.3	27.2	.0030	.0000
	.0030	25.0	24.6	.0030	.0000
.0050	.0050	17.5	17.3	.0051	+ .0001
	.0050	17.9	17.8	.0050	.0000
.0100	.0100	10.2	10.0	.0102	+ .0002
	.0100	10.8	10.5	.0103	+ .0003
	.0100	10.4	10.3	.0101	+ .0001

not satisfactory in those cases where the amount of potassium present in the sample was less than three milligrams, as indicated in Table III.

TABLE III
THE DETERMINATION OF POTASSIUM IN VARIOUS SAMPLES USING STANDARDS
REPRESENTING DIFFERING AMOUNTS OF POTASSIUM

Potassium present in Standards, g.	Potassium present in Samples, g.	Colorimeter readings (each value the mean of ten observations)		Potassium found, g.	Differences, g.
		Standards, mm.	Samples, mm.		
0.0015	0.0010	15.5	34.9	0.0007	-0.0003
	.0010	14.3	28.9	.0007	- .0003
	.0010	16.0	34.5	.0007	- .0003
	.0010	14.6	32.2	.0007	- .0003
.0020	.0010	9.2	30.2	.0006	- .0004
	.0010	8.5	28.9	.0006	- .0004
.0020	.0015	22.8	32.4	.0014	- .0001
	.0015	20.6	30.1	.0014	- .0001
	.0015	18.6	26.4	.0014	- .0001
	.0015	21.5	31.9	.0013	- .0002
.0030	.0015	13.3	31.0	.0013	- .0002
	.0015	14.0	34.3	.0012	- .0003
.0030	.0020	18.6	32.5	.0017	- .0003
	.0020	16.7	29.7	.0017	- .0003
.0050	.0020	11.0	33.6	.0016	- .0004
	.0020	11.7	36.2	.0016	- .0004
.0050	.0030	14.5	25.2	.0029	- .0001
	.0030	14.9	25.4	.0029	- .0001
	.0030	15.8	25.9	.0031	+ .0001
.0100	.0050	12.2	24.0	.0051	+ .0001
	.0050	12.1	24.3	.0050	.0000

This divergence can be attributed to the fact that, due to solubility, a certain constant amount of potassium picrate remains unprecipitated, an effect that yields disproportionate variations in comparing samples containing the lower amounts of potassium with standards containing considerably higher amounts and *vice versa*. This source of error can be obviated entirely by making comparisons only between samples and standards containing approximately the same amounts of potassium as recommended in the procedure. In practice it was found that the use of a series of standards containing 0.0010, 0.0012, 0.0015, 0.0020, 0.0025, 0.0030, 0.0050 and 0.0100 g. eliminates this source of error and gives results on all amounts of potassium within this range as satisfactory as those shown in Table II, especially if care is taken to compare a given sample with the higher standard in cases where the sample is found to lie between two standards in the above series. Such a series of standards appears to be quite permanent, even over a period of a year, if care is taken to guard against

loss by evaporation. This method is not suitable for the determination of amounts of potassium much greater than 0.0100 g., due to the increased difficulty in matching such intensely-colored solutions, nor is it suitable for amounts below 0.0010 g. by reason of the fact that precipitation of amounts below 0.0006 to 0.0007 g. does not occur with the volumes of test solution and reagent given in the procedure. By reducing these latter volumes in proportion, amounts below 0.0010 g. can be estimated but this modification is not advisable due to increased manipulative difficulties and to increased interference from sodium.

Effect of the Presence of Other Substances.—As pointed out in the previous paper¹ the potassium and other metals can be present only as chlorides by reason of the nature of the reagent. Sulfates can be transposed in the usual way by means of barium chloride. Small amounts of insoluble substances such as dehydrated silica and barium sulfate do not interfere. The influence of sodium and other metals likely to be associated with potassium is shown in Table IV. Experiments with ammonium, rubidium and cesium are not included in the table since these behave in practically the same manner as potassium. Such interference is not im-

TABLE IV

INFLUENCE OF THE PRESENCE OF SMALL AMOUNTS OF OTHER METALLIC CHLORIDES ON THIS METHOD FOR THE COLORIMETRIC ESTIMATION OF POTASSIUM

Element present	Amount of element present, g.	Potassium Present, g.	Potassium Found, g.	Differences, g.
Na	0.005	0.0010	0.0010	0.0000
	.006	.0010	.0009	— .0001
	.007	.0010	.0009	— .0001
	.008	.0010	.0038	+ .0028
	.009	.0010	.0052	+ .0042
Na	.005	.0050	.0048	— .0002
	.006	.0050	.0051	+ .0001
	.007	.0050	.0051	+ .0001
	.008	.0050	.0067	+ .0017
	.009	.0050	.0094	+ .0044
Li	.010	.0010	.0009	— .0001
	.010	.0050	.0050	.0000
Na	.005	.0050	.0050	.0000
Li	.005			
Mg	.005			
Ca	.005			
Ba	.005			
Sr	.005			
Li	.010	.0050	.0050	.0000
Mg	.010			
Ca	.010			
Al	.010			
Fe ⁺⁺⁺	.010			

portant, however, since ammonium is readily removed and rubidium and cesium are so rarely met with in weighable quantities. The interference from sodium is more serious and restricts the method to the examination of samples or residues weighing not more than twenty milligrams in cases where the sodium content is entirely unknown. Where the sodium content is approximately known, larger samples may, in many cases, be used. The other common metals usually associated with potassium apparently do not interfere even when present in larger amounts than shown in the typical experiments recorded in the table. This method is more particularly suitable for the rapid estimation of potassium in small residues of alkali and alkaline earth salts and is convenient where a series of determinations is to be made.

Summary

There has been described a rapid method for the colorimetric estimation of potassium depending upon its precipitation as potassium picrate by an alcoholic solution of picric acid with the subsequent solution of the separated precipitate in water, yielding a highly-colored solution suitable for colorimetric comparison with standard solutions prepared in a like manner from known amounts of potassium.

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ELECTRIC MOMENT AND MOLECULAR STRUCTURE. II. TERTIARY BUTYL AND TRIPHENYLMETHYL CHLORIDES AND ALCOHOLS

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In an earlier paper¹ it has been shown that the relation between electric moment and chemical behavior is usually slight, but it has seemed desirable to pursue the investigation further for the case of a few closely related groups of markedly different chemical behavior. For this purpose, the *n*-butyl, *tert.*-butyl, and triphenylmethyl groups seemed particularly suitable. The *n*-butyl alcohol² and chloride³ having already been investigated, the corresponding *tert.*-butyl and triphenylmethyl compounds were measured. While the determinations were being made, Parts⁴ published values for the moments of the primary, secondary and tertiary butyl halides, which will be used in the subsequent discussion. It was hoped that the polariza-

¹ Smyth, *THIS JOURNAL*, **51**, 2380 (1929).

² Miles, *Phys. Rev.*, **34**, 964 (1929); Smyth and Stoops, *THIS JOURNAL*, **51**, 3312 (1929).

³ Smyth and Rogers, *ibid.*, **52**, 2227 (1930).

⁴ Parts, *Z. physik. Chem.*, [B] **7**, 327 (1930).