from the U-tubes at the conclusion of the experiments and were immersed in water. In each case immediate evolution of hydrogen was observed.

Tin.—A weighed sample of tin was kept in contact with a solution of ammonium trinitride in liquid ammonia for four hours. No action was observed to take place, and the presence of tin in the residual solid after the metallic sample had been removed could not be detected.

Summary.

In the present investigation it has been shown that:

1. Metallic lithium, sodium, potassium, calcium, and magnesium react vigorously with a liquid ammonia solution of ammonium trinitride, with formation of the respective trinitrides and with liberation of ammonia and hydrogen in accordance with the general equation given by Franklin.
2. Zinc does not react perceptibly with ammonium trinitride in liquid ammonia. In contact with platinum, however, a very slow reaction takes place.
3. Aluminium (both ordinary and active) and tin undergo no perceptible reaction when brought into contact with a solution of ammonium trinitride in liquid ammonia.

In order to facilitate the gasometric study of such reactions as the foregoing, a modified Schiff nitrometer has been designed, in which (*a*) weighed amounts of two solids may be brought together in liquid ammonia in the absence of air and moisture, (*b*) the evolved gases may be collected, measured, and preserved for subsequent analysis, and (*c*) the residual solid may be weighed and preserved or prepared for analysis.

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POTASSIUM: ITS TITRIMETRIC ESTIMATION IN SMALL AMOUNTS.

BY LEON T. BOWSER.

Received August 29, 1911.

There are in present use two colorimetric methods for the estimation of small quantities of potassium. One depends upon the red color developed by a potassium iodide solution to which potassium chloroplatinate is added, the other upon the yellow color developed by stannous chloride under the same conditions. Both are unduly sensitive to exterior conditions and even with the greatest of care it is very often impossible to obtain satisfactory results. The writer knew of a case where a set of determinations was spoiled by fumes from a fresh coat of paint in the room. While in some few laboratories no difficulties are encountered, in numerous others neither of these methods can be used; hence there is need of one indifferent to any but the most unusual of exterior conditions.

After the development of the qualitative method described in the previous paper[1] an effort was made to apply it to quantitative work. The reaction does not lend itself either to colorimetric or turbidity methods on account of the very dark color of the reagent, and several other plans also failed. A method was finally worked out, involving precipitation of potassium as dipotassium sodium cobaltinitrite, filtering under appropriate conditions, and titrating the precipitate by means of very dilute potassium permanganate. After working out the proper conditions this procedure proved very satisfactory.

Among other things the cobaltinitrite method, as applied to larger amounts, calls for evaporation of the potash solution with excess of the reagent, but for several reasons this is not advizable with small amounts of potassium. Evidently there was needed a way of throwing down the yellow triple nitrite without evaporation, and of accurately measuring its amount after precipitation. Before finding just the requisit conditions numerous tests were made and many interesting facts were learned. Thus it was found that if to a potassium solution there be added strong acetic acid, then reagent, no precipitate appears, but when the reagent is added first, followed by acetic acid, a very good precipitate is obtained.

It was also found that certain reagents, notably alcohol and glacial acetic acid, act as accelerating agents, rendering the precipitation rapid and more or less complete. Alcohol alone gives complete precipitation when added to a mixture of potash solution and sodium cobaltinitrite reagent, but the precipitate is in such a finely divided condition as to render filtration extremely difficult and washing nearly impossible on account of the tendency to run through the filter. Titration results are high and evidently the conditions of precipitation abnormal, since consistent results are not obtainable. With acetic acid, on the other hand, the precipitate is of a coarse, granular nature and gives not the slightest hint of difficulty in washing. Unfortunately, however, precipitation is incomplete and far from uniform, while at the same time there is fairly rapid decomposition of both precipitate and reagent upon standing for a short period. There seems to be no other reagent answering the requirements as satisfactorily as either of these.

A study of the peculiarities of behavior of each of these reagents shows that they are supplementary, so to speak, alcohol giving complete precipitation and acetic acid incomplete, alcohol a poor texture of precipitate and acetic acid a very good one. This indicated that a mixture of the two might combine their good qualities, and trials showed such to be the case. The best results are attained when the mixture contains equal parts of glacial acetic acid and 95 per cent. alcohol, designated for the sake of convenience as acid-alcohol.

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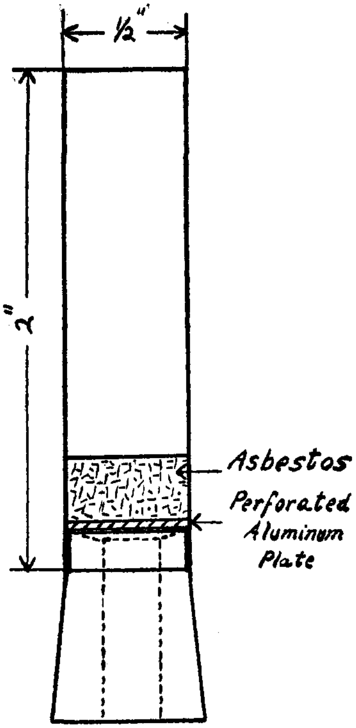
[1] THIS JOURNAL, 33, 1566 (1911).

The minimum quantity of precipitating reagent allowable was found to be about 2.5 cc.; larger volumes do no harm but smaller ones give incomplete precipitation. The precipitating reagent dipotassium sodium cobaltinitrite, is prepared as described in numerous other papers,[1] and the details are unnecessary here.

The technic of the method finally adopted is as follows: The solution in which potassium is to be determined is evaporated nearly to dryness in a beaker, cooled, and to it added 2.5 cc. of sodium cobaltinitrite solution and 10 cc. of acid-alcohol, followed by agitation of the beaker. The precipitate is filtered under suction, not allowing it to remain for more than half an hour in contact with the reagent. The filter used is of the Shimer form, the dimensions being given in the figure. The excess of reagent is washed out by means of 20 per cent. acetic acid.



The asbestos pad bearing the precipitate is now pushed out into the beaker in which the precipitation was made, the filter tube rinsed with a few cc. of water, and the aluminum filter plate taken out and rinsed. An excess of 0.005 *N* potassium permanganate is run in, the solution is brought to boiling accompanied by stirring and the nitrous acid of the precipitate released by means of 1 cc. of sulfuric acid (1 part conc. acid : 1 part water). Heating and stirring are continued for a moment, then the excess of permanganate is titrated back by means of 0.005 *N* oxalic acid, if necessary adding more permanganate to get the end-point. After deducting a blank for asbestos, sulfuric acid, etc., the number of cubic centimeters of permanganate used, multiplied by 0.00004282, gives grams of K_2O, or by 0.00003554 gives grams of K.

A considerable portion of the procedure for potassium was subsequently adapted to the estimation of calcium, and the details of the latter method have already been published.[2] In that paper is given a full description of the burets used and of the titration blank on asbestos, but to avoid

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[1] Adie and Wood, *J. Chem. Soc.*, **77**, 1076. Sutton, "Volumetric Analysis," ninth edition, pp. 61–3. Bowser, *J. Ind. Eng. Chem.*, **1**, 791.

[2] *J. Ind. Eng. Chem.*, **3**, 82 (1911).

the necessity of referring back, such of the description as pertinent will be quoted.

"All titrations are carried out with the titrated solution kept at nearly the boiling point. With a little practice the end-point of this reaction may be noted easily and with precision. From the results of the titration, a blank, to be determined by a separate titration, must be deducted as an allowance for permanganate consumed by the asbestos, water and sulfuric acid used. The first blank titration of a pad of asbestos oxidizes out practically all the impurities," and subsequent titrations establish the real blank to be deducted. "Practically all of the permanganate consumed is due to the 1 cc. of sulfuric acid used, as ascertained by a number of trials, hence there is necessity for care that exactly the same amount be used every time."

In the case of the calcium method practically the same amount of permanganate is used up in successive blanks, and the tenth titration will give about the same as the second. It is not so with the potassium method; there are considerable differences between successive titrations and these differences follow no rule whatever, hardly ever being twice the same. For this reason it is necessary to carry out a blank titration on the asbestos before each filtration. In actual analytical practice the asbestos from a preceding determination is poured into the filter tube made into a pad, and well washed with distilled water or 20 per cent. acetic acid. It is then rinsed into a beaker and titrated as in a determination, after which it is again made into a pad and used for filtering the potassium precipitate, the results of the blank titration being afterward subtracted from those obtained in the titration of the precipitate. This procedure, if judged from the written description, might appear to be bothersome and time-consuming, but it is in reality very simple and quickly carried out, as a few trials will prove.

The burets used in this titration are more strictly cataloged as graduated pipet. "For the most accurate work a small one graduated in fiftieths or hundredths is to be preferred, and this may, if desired, be read to two-hundredths of a cc. There is in use here a 2 cc. size graduated in fiftieths for permanganate, and a 1 cc. graduated in hundredths for oxalic acid. Both are fitted with tips drawn out so fine that the drops are very small, a size such that ten drops of solution equal 0.15 cc. is very satisfactory. A short rubber tube between the buret and small tip, with a glass bead in the tube to take the place of the more usual stopcock, gives a very delicate and satisfactory control of the rate of flow. The buret is filled by inserting the tip in the desired solution and drawing it up by suction, taking care to avoid contamination in any way."

In Table I are shown the results from a number of titrations on potassium salts alone. Figures are parts per million of potassium.

TABLE I.

Calculated.	Found.	Calculated.	Found.	Calculated.	Found.	
25.00	26.13	7.12	6.62	1.000	0.854	*a*
	24.92		6.80		0.710	
	26.25		7.21		1.150	
	26.32		6.76		0.783	
	25.37		6.71		0.815	*b*
	24.56		7.63		0.822	
	24.52		6.99		0.815	
	25.48		7.69		0.861	
Av.....	25.44		7.05		0.874 (*a*) 0.828 (*b*)	

(*a*) using 10 cc. K solution
(*b*) using 50 cc. K solution

On the whole these results are quite satisfactory considering the small amounts involved.

To test the method in the presence of other metals, determinations were made in which potassium, sodium, calcium and magnesium were present in equal amounts. The results are shown in Table II, figures being parts per million as before.

TABLE II.

Calculated.	Found.	Calculated.	Found.	Calculated.	Found.
50.00	50.57	20.00	20.57	3.50	3.70
	51.20		20.04		3.27
	51.66		20.48		3.27
	48.05		...		..
Av.........	50.37		20.36		3.45

The presence of these metals has no appreciable effect on the amount of potassium found by titration, at least not when in moderate amounts.

Attempts were made to compare this method with the colorimetric one using potassium iodide, but unfavorable exterior conditions made it impossible to secure results by the latter. By the titration method very consistent results were obtained, the unfavorable conditions seemingly failing to affect it. So far as found the only difficulty encountered is when heavy ammoniacal fumes are in the air, and as a matter of ordinary precaution no estimations should be undertaken under such conditions.

Very satisfactory duplicates are obtainable by this method, and it is hoped that it may be found much better adapted to ordinary laboratory conditions than the colorimetric methods. It is very simple, the manipulations are few and easy, and the results are dependable. In concluding, it may well be noted that up to the present all attempts to apply this or any similar procedure to the estimation of larger amounts of potassium have proved futil.

DAYTON, O

THE INFLUENCE OF THE MAGNETIC FIELD ON PASSIVE NICKEL AND IRON.

BY HORACE G. BYERS AND AGNES FAY MORGAN.

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In a previous article[1] it was shown that when using iron as an anode in various electrolytes the density of the current required to produce the passive condition is very materially increased when the anode is placed in a magnetic field. The amount of current required varied not only with the intensity of the field but also with different electrolytes and with the length of time of exposure of the iron to the electrolyte and perhaps with other factors; but in every case the required current density per square centimeter was greater in the magnetic field than out of it. A natural development of this work was an investigation of similar nature with nickel and steel as anodes.

In view of the rather rare instances of magnetic effects upon chemical action a brief summary of the literature of the subject may be in place. So far as we are aware the first contribution was by Professor Remsen[2] who showed that iron in a solution of copper sulfate is protected at the ends when in a magnetic field. Rowland and Bell[3] explain the action on the supposition that more energy is required to remove the iron from points nearest the magnetic poles induced by the magnetic field. They also present experimental evidence in support of their conclusion. Wolff[4] explains the protection on the basis of an accumulation of iron salts at the magnetic poles.

The articles cited all deal with a *protection* of iron from chemical action by magnetization. On the other hand Nichols and Franklin in a series of articles[5] call attention to the destruction of the passive condition of iron, when in concentrated nitric acid, by means of a magnetic field and take issue with the explanations offered by Rowland and Bell.[6] Andrews[7] showed that magnetized steel and unmagnetized steel show differences of potential in nitric acid (sp. gr. 1.42) of approximately 0.03 volt, at low temperatures the magnet being positive, while at 90° the voltage

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[1] Byers and Darrin, THIS JOURNAL, 32, 750 (1910).

[2] *Am. Chem. J.*, 3, 157 and 6 (1881 and 1885).

[3] *Am. J. Sci.*, [3] 36, 39 (1888).

[4] *Am. Chem. J.*, 17, 122 (1895).

[5] *Am. J. Sci.*, [3] 31, 272 (1886); [3] 34, 419 (1887); [3] 35, 290 (1888).

[6] *Loc. cit.*

[7] *Proc. Roy. Soc. London*, 48, 116 (1891).