ART. XVII.—*A method for the Iodometric Determination of Nitrates;* by F. A. GOOCH and H. W. GRUENER.

[Contributions from the Kent Chemical Laboratory of Yale College—XV.]

IT has been shown by DeKoninck and Nihoul* that nitrates may be decomposed completely by the prolonged action of gaseous hydrochloric acid, and determined with accuracy by measuring the iodine set free when the products of decomposition, carefully kept from atmospheric contamination, act upon potassium iodide. These investigators recognized the difficulties attending the use of gaseous hydrochloric acid in analytical processes, and endeavored unsuccessfully to substitute the strong aqueous solution for the gaseous acid. The work to be described in the following account was performed in the search for a simpler method for the iodometric determination of nitrates.

According to a process recently developed in this laboratory† chloric acid may be determined with the greatest ease. It was shown that in the interaction of a chlorate with potassium iodide, arsenic acid, and sulphuric acid, in regulated quantities in aqueous solution and at the boiling temperature, the first action of the hydriodic acid set free from the iodide by the sulphuric acid is upon the chloric acid, and that not until this action is completed is the arsenic acid attacked and reduced with the simultaneous liberation of a corresponding amount of iodine. If the arsenic acid is taken in quantity sufficient to insure the final decomposition of the entire amount of iodide present, the arsenious acid found at the end of the action is an exact measure of the amount of iodide which escaped the action of the chlorate; and, the quantity of iodide originally taken being known, the amount acted upon by the chlorate, and so the amount of the chlorate itself, becomes known. The arsenious acid is determinable with great accuracy iodometrically, and the chief advantage of the process lies in the fact that the titration is made upon the residue, and that, no collection of the distillate being necessary, the sole apparatus employed in the process proper is an Erlenmeyer beaker and a bulbed tube hung in its neck as a trap to prevent mechanical loss.

This process we endeavored to apply to the determination of nitrates, but under none of the many variations of form and changes of conditions under which we tested it, were we able to secure complete decomposition of the nitrate without so

* Zeitschr. für angewandte Chemie, 1890, p. 477.
† Gooch and Smith, this Journal, vol. xlii, p. 220.

increasing the strength of the sulphuric acid that it was acted upon by hydriodic acid with the consequent unregistered escape of products of decomposition.

The endeavor to substitute a process essentially similar in principle, in which hydrochloric and antimonic acids should replace the sulphuric and arsenic acids proved likewise unsuccessful.

Abandoning therefore all attempts to so arrange the process that the oxidizing action of the nitrate should be registered in the residue, search was made for a reagent which should be capable of inducing easy decomposition of nitrates (after the manner of ferrous salts in acid solution) and yet (unlike ferrous salts) should be so readily restored to its primitive condition that the products of the oxidizing action of the nitrate should finally pass entirely to the distillate and be registered there. We have found the desired combination of qualities in manganous chloride dissolved to saturation in concentrated hydrochloric acid. This reagent is acted upon but slowly by nitrates at the ordinary temperature, but upon warming the nitrate begins at once to decompose with the formation of a higher chloride of manganese and liberation of nitric oxide. Ultimately if the heating is continued the chlorine of the higher chlorides is evolved and manganous chloride remains. During the process of heating the color of the solution passes from the original characteristic green through darker shades to black and returns by the reverse changes to the original tint. The decomposition of the nitrate extends under the conditions to the last traces, but the breaking up of the nitrates with the formation of the higher chloride, does not take place completely in the presence of water amounting to more than a third of the volume of the solution, and an action already established in strong acid is reversed by the addition of a large amount of water. Chlorates, peroxides, and other substances which liberate oxygen or chlorine when in contact with strong hydrochloric acid induce similar phenomena, but in the absence of such other substances the reaction serves to detect nitrates when present in fairly small amounts (perhaps one part in sixty thousand) as shown in the accompanying table :

KNO_3 taken.	$MnCl_2 . 4H_2O$ in strong HCl	Color developed.
0·01000 grm.	10 cm^3	Black.
0·00500	5	Black.
0·00100	5	Dark brown.
0·00050	5	Dark green.
0·00025	5	Deepened tint.
0·00015	5	Deepened tint.
0·00005	5	None.
0·00000	5	None.

In the first attempts to apply this reaction to the quantitative estimation of nitrates, 10 cm³ of the manganous mixture, the pure weighed nitrate, and an excesss of potassium iodide were put in a tubulated retort fitted with a hollow ground stopper drawn out at both ends so as to serve for the introduction of carbon dioxide evolved in a Kipp's generator charged with marble and acid previously boiled. The neck of the retort passed through a rubber stopper nearly to the bottom of a side-neck Erlenmeyer flask, used as a receiver, in the mouth of which the stopper fitted tightly. The side-neck of the receiver was joined by a rubber connector with a bent glass tube passing through a rubber stopper and reaching nearly to the bottom of a side-neck test tube into the mouth of which the stopper was fitted.

The first receiver contained hydrogen sodium carbonate in excess of the amount needed to neutralize the acid in the retort as it should distil over, a considerable quantity of potassium iodide (about 3 grm.) to aid in dissolving condensed iodine, and arsenious oxide in known amount and in excess of the quantity necessary to convert to hydriodic acid the free iodine evolved. The second smaller receiver was partly filled with a dilute solution of potassium iodide and hydrogen sodium carbonate. The current of carbon dioxide was started immediately upon introducing the contents of the retort, and the air was safely removed before the darkening of color, which begins to appear very soon, had spread through the liquid. Heat was applied, and the evolution of nitric oxide and later that of iodine began. The distillation was continued until nearly all the liquid had passed over. Finally, the contents of both receivers were united and titrated against decinormal iodine. The excess of arsenious oxide remaining unoxidized was taken as the measure of the iodine liberated and, accordingly, of the nitrate decomposed, upon the presumption that two molecules of the nitrate liberate ultimately six atoms of iodine according to the equation

$$2HNO_3 + 6H\text{-}I = 4H_2O + 2NO + 3I\text{-}I.$$

The choice of the solution for the retention of the halogen evolved was dictated by the consideration, in the first place, that very little iodine could pass through the alkaline arsenite to come into contact with the rubber stopper of the receiver on the way to the second absorbing liquid, and, secondly, that higher oxides of nitrogen reformed by the action of traces of air possibly introduced with the carbon dioxide or imperfectly removed by it could not liberate iodine from an iodide in in alkaline solution.

The iodide was introduced into the retort because having chosen to collect the halogen in alkaline solution it became necessary to take steps to break up, before it should reach the receiver, all nitrosyl chloride, the formation of which our experience in former lines of work not here detailed had led us to expect under the circumstances. In acid solution containing an iodide, nitrosyl chloride liberates iodine and is registered; in alkaline solution it breaks up with the formation of a chloride and a nitrite, the latter having no immediate action upon the arsenite. The results of experiments made in this manner are recorded in the accompanying table.

TABLE I.

KNO_3 taken.	KI in retort.	$MnCl_2$ mixture.	KNO_3 found.	Error.
0·1036 grm.	0·8 grm.	10 cm^3	0·1009 grm.	0·0027 grm. —
0·1083 "	0·8 "	10 "	0·1082 "	0·0001 " —
0·1064 "	0·8 "	10 "	0·1053 "	0·0011 " —
0·1068 "	0·8 "	10 "	0·1033 "	0·0035 " —
0·0551 "	0·8 "	10 "	0·0531 "	0·0020 " —

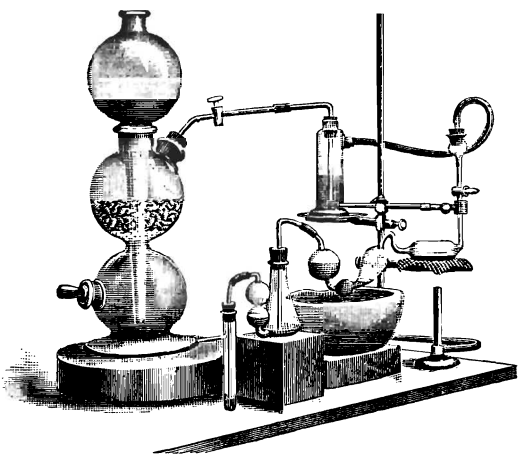
The experiments of Table II were carried out in a manner essentially similar to that of the experiments of Table I, excepting the single point that the iodine evolved in the process of decomposition of the nitrate was received in potassium iodide instead of in an alkaline arsenite. The contents of the receivers were united, made alkaline with hydrogen sodium carbonate, treated with an excess of decinormal arsenious acid, and the unoxidized arsenious acid was determined by decinormal iodine.

TABLE II.

KNO_3 taken.	KI in retort.	$MnCl_2$ mixture.	KNO_3 found.	Error.
0·2039 grm.	1·6 grm.	20 cm^3	0·2025 grm.	0·0014 grm. —
0·1060 "	0·8 "	10 "	0·1035 "	0·0025 " —
0·1036 "	0·8 "	10 "	0·1016 "	0·0020 " —
0·1013 "	0·8 "	10 "	0·1002 "	0·0011 " —
0·0521 "	0·5 "	10 "	0·0521 "	0·0000 " —
0·0235 "	0·5 "	5 "	0·0227 "	0·0008 " —
0·0273 "	0·5 "	5 "	0·0262 "	0·0011 " —
0·0136 "	0·2 "	5 "	0·0132 "	0·0004 " —
0·0011 "	0·2 "	5 "	0·0009 "	0·0002 " —

The errors of both sets of experiments, those of Table I and those of Table II, are considerable, all lie in the same direction, and are indicative of too low registering of the action of the nitrate, since of the complete decomposition of

the nitrate there can be no reasonable doubt in view of the proved behaviour of the manganese salt toward small amounts of nitrates. To us it seemed probable that the explanation of these results was to be sought in the failure of the titration in alkaline solution to indicate completely all the final products of the action of the nitrate. The formation, even in small amounts, of compounds of nitric oxide with iodine analogous to those which we know to be formed with bromine and chlorine, or the partial reoxidation of the nitric oxides by the action of iodine with the aid of water, an action which we recognize as possible under certain conditions of dilution, would account satisfactorily for the deficiency in the results of titration effected in alkaline solution. Upon this presumption the simple and obvious modification of titrating in acid solution should correct the error. Accordingly in the following series of experiments the plan of collecting the halogen and titrating in alkaline solution was abandoned, and since the addition of an iodide to the retort was no longer essential this practice was discontinued. The products of the action of the nitrate upon the manganese mixture—chlorine, nitric oxide and perhaps nitrosyl chloride,—were received directly in potassium iodide, and the iodine set free was titrated by sodium thiosulphate, itself standardized against iodine of known value with respect to a standard solution of decinormal arsenious oxide.



With the abandonment of the plan of putting the alkaline arsenite into the receiver the tendency of the iodine to pass onward to the second receiver is augmented and the possible action of the rubber stopper of the receiver becomes corre-

spondingly dangerous. We modified the apparatus, therefore, so that only glass should occur where by any possibility rubber connections might act upon the free halogen. In place of the ordinary retort we adopted a form of apparatus made use of formerly by one of us in the quantitative distillation of boric acid under the action of methyl alcohol—a pipette bent and fitted as shown in the figure. To this apparatus was sealed a Varrentrapp and Will nitrogen bulb, the exit tube of which was drawn out so that it might be pushed well within the inlet tube of the second receiver—a Will and Varrentrapp absorption flask—and held in place by an outside rubber connector. The third receiver acts simply as a trap to exclude air from the absorption apparatus proper. In conducting the experiment the receivers were charged with solutions of potassium iodide, the first containing three grams, the second one gram, and the third only a fraction of a gram for every tenth of a gram of nitrate used. The first receiver was kept cool during the process by immersion in water. The introduction of the nitrate and manganous mixture following it was made easy and safe by applying gentle suction to the end of the absorption train. The current of carbon dioxide was started immediately after putting in the manganous mixture, and after a suitable time had elapsed for the removal of air heat was applied to the retort and the distillation was continued until nearly all the liquid had passed over. Finally the contents of the receivers were united, the washing of the bulbs was effected easily and expeditiously by passing the wash-water directly through retort and receiver (the introduction of the manganese chloride into the distillate being not at all prejudicial to the accuracy of the titration), and the estimation of free iodine made by sodium thiosulphate as described. The results of the experiments conducted in this manner are given in Table III.

These results are fairly satisfactory. The mean error of the entire series is practically nothing. The manipulation is easy and rapid.

In brief, the process which gives us these results consists in the distillation of the mixture of the nitrate with a saturated solution of crystallized manganous chloride in strong hydrochloric acid in an atmosphere of carbon dioxide, the passage of the products of action into potassium iodide, and the titration of the liberated iodine by sodium thiosulphate. It is important to take precautions to prevent the contact of the free halogen with rubber stoppers or connectors, and any apparatus, suitable for ordinary quantitative distillation and absorption, which meets this condition will probably answer the requirements of the process. Our own preference is for the apparatus described and figured.

TABLE III.

KNO_3 taken.	$MnCl_2$ mixture.	KNO_3 found.	Error in terms of KNO_3.	Error in terms of HNO_3.
0·2038 grm.	20 cm³	0·2047 grm.	0·0009 grm. +	0·0005 grm. +
0·2053 "	20 "	0·2057 "	0·0004 " +	0·0003 " +
0·1032 "	10 "	0·1035 "	0·0003 " +	0·0002 " +
0·1017 "	10 "	0·1004 "	0·0013 " —	0·0008 " —
0·1049 "	10 "	0·1049 "	0·0000 "	0·0000 "
0·1027 "	10 "	0·1023 "	0·0004 " —	0·0003 " —
0·0524 "	10 "	0·0526 "	0·0002 " +	0·0001 " +
0·0513 "	10 "	0·0512 "	0·0001 " —	0·0001 " —
0·0354 "	10 "	0·0350 "	0·0004 " —	0·0003 " —
0·0232 "	10 "	0·0230 "	0·0002 " —	0·0001 " —
0·0107 "	5 "	0·0106 "	0·0004 " —	0·0001 " —
0·0127 "	5 "	0·0130 "	0·0003 " +	0·0002 " +
0·0145 "	5 "	0·0143 "	0·0002 " —	0·0001 " —
0·0053 "	5 "	0·0052 "	0·0001 " —	0·0001 " —
0·0043 "	5 "	0·0047 "	0·0004 " +	0·0003 " +
0·0014 "	5 "	0·0018 "	0·0004 " +	0·0003 " +
0·0000 "	5 "	0·0000 "	0·0000 "	0·0000 "

The titration should be completed as soon as may be after admitting air to the distillate in order that traces of dissolved nitric oxide may not be reoxidized and again react upon the iodide present to liberate more iodine.