[Contribution from the Explosives Chemical Laboratory, Bureau of Mines.]

"NITRON" AS A GRAVIMETRIC REAGENT FOR THE ANALYSIS OF SUBSTANCES USED IN EXPLOSIVES.*

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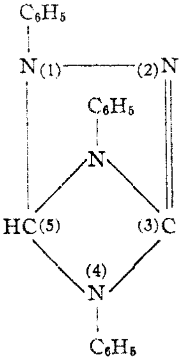
The object of this paper is to collect the rather scattered information regarding "nitron" and its applications, add to it the work done in the laboratory of the Pittsburgh station of the Bureau of Mines, and compile the matter in a comprehensive form that will enable one intelligently to make a hasty survey of the subject. This, we trust, will lead to further investigations and result in the use of "nitron" for many analyses which at present are rather involved.

"Nitron" discovered by Busch[1] is the commercial name given to 1,4-diphenyl-3,5-endoanilodihydrotriazol. Its formula is $C_{20}H_{16}N_4$ or



It is a basic substance forming salts with acids, a great number of which are practically insoluble in water. It is soluble in alcohol, benzene, chloroform, acetone, acetic acid, and acetic ether, slightly soluble in ether, and almost insoluble in water. Owing to its high molecular weight (312.2) it is particularly adapted as a gravimetric reagent for the compounds with which it forms practically insoluble salts. Busch[2] gives the solubilities of the following addition products, which "nitron" forms with acids: Bromide (1 in 800), iodide (1 in 20,000), nitrite (1 in 4,000), chromate (1 in 6,000), chlorate (1 in 4,000), perchlorate (1 in 50,000), nitrate (1 in 60,000). He[16] also states that "nitron" picrate is practically insoluble in water (1 in 250,000). Visser[13] claims that oxalic and salicylic acids also form insoluble precipitates. Sulfuric, hydrochloric, formic, acetic, boric, benzoic, tartaric, citric and phosphoric acids yield soluble salts. Visser has also applied "nitron" as a microscopic reagent for distinguishing many of its slightly soluble salts.

"Nitron," however, has found its most general application as a gravi-

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metric reagent for nitric acid and its salts. Busch[8] recommends the use of "nitron" for the estimation of organic nitrates, and nitric esters. Utz[15] gives a method for the analysis of picric acid which is with slight modifications similar to that of Busch for nitrocellulose. Utz gives results for picric acid varying from 14.21% to 17.06% N as compared with the theoretical of 18.34% N. Because of the fact that his samples were not entirely water-free, definite conclusions cannot be drawn as to the accuracy of these determinations; for no standard is given with which to compare them. Since these were the only references that could be found regarding the application of "nitron" to nitric esters or nitro-compounds, these methods were investigated further to see how general their application could be made.

Several investigators have experimented on the effects of other substances on this method of determination of nitrates. Paal and Ganghofer[23] found that dextrin, even if present to the extent of 2%, does not interfere with the complete precipitation of "nitron" nitrate, if enough time is allowed. Peptone interferes to some extent, but its influence may be overcome by adding a sufficiency of sulfuric acid. It may be removed from the solution by heating on the water bath for several hours, after adding formaldehyde, and the results of the "nitron" precipitation are then quite satisfactory. Gelatin if present to the extent of less than 0.5% does not interfere. It may be removed from the solution by the addition of tannin, the excess of which is then precipitated by means of normal lead acetate. A cold water extract of meat may be analyzed for nitrates after removing the interfering substances by the addition of normal lead acetate to the boiling solution; if alkaline, some acetic acid should be added. Hes[17] states that the presence of aluminum sulfate, magnesium sulfate, ammonium sulfate, potassium phosphate, magnesium chloride, tartaric acid, citric acid, sucrose and dextrose are without influence on the precipitation of "nitron" nitrate. When oxalic acid is present, the results obtained are too high. (Paal and Ganghofer, cited above, avoid the effect by the addition of H_2SO_4.) Chloric acid precipitates "nitron" quantitatively as "nitron" chlorate if the solution contains about 0.25% of chloric acid. Nitric acid and chloric acid may be determined together in the same solution if the amount of one of the acids is known. In this laboratory the effect of chloric acid is overcome by reduction with SO_2 or formaldehyde.[26] Adan[12] states that, if nitrites are present, the results obtained are high by an amount which does not correspond with the content of nitrite. Busch[7] analyzes a mixture of nitrites and nitrates, by first determining the nitrites by oxidation with permanganate and then precipitating the total nitrate in a separate portion as "nitron" nitrate after oxidation of the nitrite with hydrogen peroxide. Franzen and Löhman[18] comment on this method as follows:* "The usual volumetric methods for the estimation of a mixture of nitrous and nitric acids are inapplicable to bacteriological cultures; good results are obtained with 'nitron.' Busch's method is used, in which the total nitric acid is estimated after the nitrous acid has been oxidized to nitric acid by hydrogen peroxide, and the residual nitric acid determined after decomposition of the nitrous acid by hydrazine sulfate."

"The estimation in the presence of 'bouillon solution' gives too low results, owing to the retention of some 'nitron' nitrate in colloidal solution. If this is prevented by the addition of 2 to 2.5 cc. of concentrated H_2SO_4 per 200 cc. of solution, the estimation in the presence of 'bouillon solution' is as accurate as in water only. Since oxalic acid is a common constituent of bacteriological cultures, the presence of sulfuric acid has an additional advantage of preventing the precipitation of 'nitron' oxalate. A somewhat large excess of 'nitron' should be used."

Many modifications have been advocated for nitrate determinations by "nitron" by various investigators and indeed some have discarded this reagent because they were unable to get satisfactory results. "Nitron" has been used in this laboratory for several years and some of the most accurate determinations of nitrates have been made with it. The method found most suitable for our work is very similar to the one proposed by Gutbier[3] and previously reported in one of this Bureau's publications.[26]

Preparation of Reagent.

To prepare the reagent one gram of "nitron" is dissolved in 10 cc. of 5% acetic acid (heating is unnecessary); the solution is filtered through an alundum crucible and placed in a dark bottle. The solution decomposes in the light and does not keep well, hence it is best to prepare it in small quantities as needed.

Determination of Nitrates.

To the solution of nitrate, containing preferably not over 0.10 to 0.15 g. of nitrate, diluted to about 80 cc., add 12–15 drops of H_2SO_4 (2 acid to 3 water), heat to the boiling point, add 10–12 cc. of the "nitron" solution, stir, and let stand $^1/_2$ to $^3/_4$ of an hour. Long, silky, needle-like crystals of "nitron" nitrate separate out on cooling. Place the beaker in ice water for $1^1/_2$ hours and filter the crystals on a Munroe or Gooch crucible, using slight suction. Use part of the filtrate for washing out the beaker. Wash the precipitate with a total of 10 cc. of ice water, in 2 cc. portions and dry at 105° for one hour, which is usually sufficient to insure complete dryness. To confirm complete precipitation heat the filtrate to boiling, add a little more of the reagent, and cool the mixture as before.

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* Taken from abstract, *J. Chem. Soc.* The English abstractors have made a curious error in referring to the "Bouillon Lösung" of the original as Bouillon's solution.

The molecular weight of "nitron" is 312.2, of "nitron" nitrate 375.2. Thus the nitrate being six times as heavy as HNO_3, an error in the weight of the precipitate is reduced to one-sixth when expressed as HNO_3, or to $^1/_{27}$ when expressed as nitrogen.

Saponification of Nitric Esters.

The nitric esters of importance used as explosives are the polynitrates of certain polyatomic alcohols. The polynitrates of glycerol, mannite, and in fact most of the common nitric esters have been branded with the misnomer of nitroglycerin, nitromannite, etc. Common practice sanctions the use of these misnomers and they are accordingly used in this paper.

When nitric esters are saponified they readily split off the nitrate groups. The alcohols, however, reduce the nitrate to nitrite* and probably under certain conditions are reduced as far as ammonia. To overcome the reducing action of the alcohols and at the same time to effect a complete conversion of all the nitrogen into nitric acid, it is necessary to use a strong oxidizing agent.

In the method worked out by Busch 3% hydrogen peroxide is used for this purpose. The procedure as given by Busch and used in this work may be briefly stated as follows:

About 0.2 g. of nitrocellulose is introduced into a 100 cc. Erlenmeyer flask, and 5 cc. of 30% aqueous caustic soda and 10 cc. of 3% hydrogen peroxide are added. The solution is heated on the water bath until frothing ceases, and then heated over a free flame to complete solution. 40 cc. of water and another 10 cc. of 3% hydrogen peroxide are then added and the liquid is heated to 50°. By means of a pipet 40 cc. of 5% sulfuric acid (sufficient to make the solution acid) are delivered at the bottom of the flask. The solution is heated just to boiling, and

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* Sidgwick in "Organic Chemistry of Nitrogen," page 9, makes the following statement in regard to nitroglycerin: "On (*b*) saponification (Robertson, *Chem. News*, 99, 289 (1909)) the NO_3 groups are readily split off as nitric acid, but they oxidize the glycerol, and are themselves reduced to nitrous acid."

As there seemed some doubt as to whether metallic nitrates when once formed could be reduced to nitrous acid by the polyatomic alcohols, a simple direct experiment was made to determine this point. Three solutions were made up as follows:

1. Sodium nitrate, sodium hydroxide, glycerol, and water.
2. Sodium nitrate, sodium hydroxide, and water.
3. Sodium hydroxide, glycerol, and water.

Each solution was boiled for a few minutes, acidified with hydrochloric acid and tested with potassium-iodide starch test paper. The paper immersed in solution No. 1 was the only one which turned blue, the ones immersed in solutions Nos. 2 and 3 remained unchanged. The same experiment was tried with mannite in place of glycerol, with similar results.

This certainly leaves no doubt that certain alcohols will reduce sodium nitrate to sodium nitrite. From qualitative tests it appears, however, that the alcohols will not reduce sodium nitrate after the metallic nitrate is once formed, to ammonia, but during saponification this probably occurs.

12 cc. of the 10% "nitron" solution are added. From this point the process is exactly the same as for nitrates.

Results obtained in this laboratory by this method for nitric esters are given in the following table:

DETERMINATION OF NITROGEN IN NITRIC ESTERS.

Substance.	Per cent. nitrogen found by "nitron."	Per cent. nitrogen found by nitrometer.
Nitrocellulose	13.13	13.15
	13.11	...
Nitromannite	18.24	18.33
	18.28	...
Nitrostarch	13.04	13.00
Nitroglycerin	17.90	18.40
	18.00	...

As may be seen from the table, the determinations by the "nitron" method for nitrocellulose, nitromannite and nitrostarch, are quite satisfactory. The results for nitroglycerin, however, are not accurate enough for practical purposes. The figure 17.90% N was consistently obtained for many determinations of nitroglycerin. On investigating this matter further, it seemed evident that the glycerol resulting from saponification, exerted a much greater reducing action on sodium nitrate than most of the other alcohols liberated from nitric esters. For a number of determinations alcoholic caustic potash was tried, but owing to the further reducing effect of the added alcohol low results were again obtained. The method finally developed, which appeared to overcome these difficulties, was to use 30% aqueous caustic soda and 30% hydrogen peroxide. The method in detail follows:

The apparatus used for carrying out the saponification consisted of a 100 cc. Erlenmeyer flask with a ground glass air condenser 25 cm. long. A sample weighing 0.1000 g. is placed in the flask. A mixture of 5 cc. 30% NaOH and 5 cc. of 3% H_2O_2 solution is added, then about 15 drops of 30% H_2O_2 are introduced. The reflux condenser is attached and the apparatus placed on the water bath. After about 10 minutes, when the evolution of gas becomes very mild, 10–15 drops of 30% hydrogen peroxide are again added. This operation is repeated over a period of 2 hours, then twice at $^1/_2$-hour intervals. By this time the small drop of nitroglycerin has disappeared from the surface and further heating on the water bath will not accomplish any further saponification. About 8% of nitrogen is converted into nitric acid up to this point.

The reflux condenser is removed, 10–15 drops of 30% hydrogen peroxide added, a small Kjeldahl connecting bulb (to prevent splashing) is inserted into the Erlenmeyer by means of a rubber stopper, and the flask is heated for a few minutes over a free flame. The addition of H_2O_2 and heating is repeated twice and the solution is finally boiled down to a volume of about 3 cc. 40 cc. of water and 10 cc. of 3% H_2O_2 are added and the liquid is heated to 50°; the solution is acidified with 40 cc. of 5% sulfuric acid and the determination is completed in the same manner as for nitrocellulose. Results obtained by this method for nitroglycerin were 18.20, 18.24, and 18.22% nitrogen as compared with 18.40% obtained by the nitrometer.

Application to Nitrocompounds.

This method was then tried on several nitrocompounds, the results of which are given in the following table:

RESULTS OF "NITRON" DETERMINATIONS ON NITROCOMPOUNDS.

	Per cent. N.		
Substance.	Aqueous NaOH 30%.	Alcoholic KOH 20%.	Theoretical (total).
Tetranitromethylaniline....	13.17	16.19	24.4
Tetranitroaniline..........	18.70	18.86	25.6
Trinitrotoluene............	14.68	15.25	18.5

These results clearly show that the decomposition of nitrocompounds quantitatively into nitric acid cannot be readily obtained by this method. The fact, however, that a large portion of the nitrogen of the nitro group is converted into the nitrate group indicates that it might be made quantitative by some variations in the method.

"Nitron" as an Aid in Differentiating between Nitrates and Nitrocompounds.

In a recent article* we called attention to the fact that the nitrometer could not be used as a means of determining whether certain substances were nitrocompounds or organic nitrates. "Nitron" precipitates nitrates as "nitron" nitrate, while with nitrocompounds it either forms no precipitates, or one which is an addition compound of "nitron" with the nitrocompound, *e. g.*, "nitrontrinitrocresolate." In the latter case the addition compound is readily distinguishable from the nitrate by the appearance of the precipitate. For specific examples urea nitrate, guanidine nitrate, nitrourea and nitroguanidine were investigated. Urea nitrate and guanidine nitrate both give precipitates of "nitron" nitrate, but nitrourea and nitroguanidine gave no precipitate.

Urea nitrate gave 11.38 and 11.37 (theoretical 11.38%) N, and guanidine nitrate 11.16 and 11.21 (theoretical 11.46%) N. The latter substance was not purified and the amounts found probably represent the true nitrogen content. "Nitron" therefore affords an additional means of differentiating between nitrates and nitrocompounds.

Determination of Picric Acid and Allied Substances.

As previously stated picric acid forms a practically insoluble addition compound with "nitron." The following method was used for this

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* THIS JOURNAL, **38**, 2552 (1916).

determination:[16] 0.2000 g. of picric acid or its salt, is dissolved in 150 cc. water and 12–15 drops of 2:3 H_2SO_4 are added. The solution is heated to boiling and 10–12 cc. of 10% "nitron" solution are added. A bright yellow precipitate forms immediately, which is allowed to cool to room temperature for about two hours. It is unnecessary to cool these compounds in ice water. The precipitate is then filtered on a Munroe or Gooch crucible, dried for 1 hour at 105°, and weighed.

As trinitrocresol is very similar to picric acid in most of its reactions, a few determinations with "nitron" were made to ascertain whether this method is applicable to trinitrocresol and its salts.

PICRATE AND TRINITROCRESOLATE DETERMINATIONS.

Substance.	Wt. gram taken.	Cc. water required for solution.	Wt. subst. found.	Remarks.
Ammonium picrate.........	0.2006	150	0.2007	C. P.
	0.2008	...	0.2008	
Trinitrocresol..............	0.1500	150	0.1502	Crystallized
	0.1500	...	0.1497	from alcohol
Ammonium trinitrocresolate.	0.1500	75	0.1465	
	0.1500	...	0.1470	Not purified

Phenol and the mono- and dinitrophenols were also tested in the above manner, but none gave a precipitate. 0.1000 g. 1,2,4-dinitrophenol dissolved in 200 cc. of water gave a copious yellow precipitate with "nitron" solution when no H_2SO_4 was added. This precipitate was filtered, washed, dried and weighed in the usual manner. Calculated on the basis of an addition product it gave 0.1009 g. dinitrophenol.

This immediately suggested a new method for the analysis of a mixture of picric acid and dinitrophenol. The following procedure was adopted:

0.1505 g. picric acid and 0.0500 g. dinitrophenol were dissolved in 250 cc. of water and heated to boiling without the addition of acid, and 12 cc. "nitron" solution were added. The mixture was cooled to room temperature for 2 hours, filtered, washed, dried at 105° for 1 hour, and weighed. This procedure was repeated on a similar sample, but with the exception that 15 drops 2:3 H_2SO_4 were added previous to boiling.

DETERMINATION OF A MIXTURE OF PICRIC ACID AND DINITROPHENOL.

	Weights taken.		Weights found.	
Conditions.	Picric acid.	Dinitrophenol.	Picric acid.	Dinitrophenol.
Acid added.......	0.1505	0.0500	0.1539	0.0000
No acid added....	0.1505	0.0500	0.1539	0.0466
	..	..	0.1505 (*a*)	0.0495 (*a*)

(*a*) Calculated.

The calculated results are given to show the almost complete insolubility of the mixed precipitates, and are obtained by deducting the theoretical weight of "nitron" picrate from the total precipitate.

Busch and Blume[15] give very good results for determining picric acid in this mixture when it is acidified with sulfuric acid. According to their results the calculated values in the table are what should be expected in these determinations. To our knowledge a more accurate method for this analysis is not known.

While this particular analysis may not be of very great importance, the method here suggested should prove a rather fertile field for investigation, especially as regards analyses of complicated mixtures.

Determination of Perchlorates.

A few determinations were carried out with commercial C. P. ammonium perchlorate by the same method as for nitrates. 0.12 g. of perchlorate was taken. Its purity by this method was found to be 99.67 and 99.58%, while by the fusion method 99.53% purity was obtained. These results were previously recorded[26] and as far as known this was the first application recorded of "nitron" for the determination of perchlorates.

Determination of Oxides and Nitrogen.

C. G. Storm, former explosives chemist of the Bureau of Mines, in March, 1910, applied "nitron" to the analysis of a mixture of gas containing NO and NO_2. Later Burrell and Seibert[30] adopted his method for the determination of oxides of nitrogen in mine air. To our knowledge no other adaptation of the "nitron" method has been applied to gas analysis.

The method may be outlined as follows: By means of a separatory funnel, 10 cc. of a 5% solution of potassium hydroxide and 10 cc. of a 3% solution of hydrogen peroxide were poured into a 2-liter bottle; the hydrogen peroxide to oxidize the nitrous fumes to nitric acid, and the potassium hydroxide to form potassium nitrate. The bottles were shaken frequently to insure complete oxidation and absorption. The solution was then washed into a beaker, the wash water being used sparingly so that the total volume of solution was not greater than 30–40 cc. The solution was then made slightly acid with 10% sulfuric acid, the solution heated to boiling and 10 cc. of "nitron" solution added. It was then cooled, filtered, and the precipitate was washed, dried and weighed in the usual manner. Theoretically 1 cc. of nitric oxide requires 0.01344 g. of "nitron," and 1 cc. of nitric oxide is equivalent to 0.0168 g. of "nitron" nitrate.

RESULTS OF GAS ANALYSIS WITH THE "NITRON" METHOD.

Sample No.	NO present. Cc.	NO found. Cc.	Sample No.	NO present. Cc.	NO found. Cc.
1	3.7	3.5	6	0.2	0.2
2	2.4	2.4	7	0.2	0.2
3	2.8	2.6	8	0.8	0.6
4	0.9	0.6	9	1.7	1.5
5	2.7	2.5			

Results obtained by Burrell and Seibert on measured amounts of nitric oxide, prepared in a Lunge nitrometer from pure nitrates, are given in the preceding table.

They comment on these results as follows:

> "It is shown from the above results that with a sufficiently large sample of mine air (5 or 10 liters) quantities of nitric oxide much below that required to produce harmful effects on men can be detected by this method."

When a mixture of NO and NO_2 are present the NO may be determined by absorption in $FeSO_4$ solution and the difference will be NO_2.

Recovery of Reagent.

"Nitron" varies in price from four to six dollars per ounce, and as its recovery is a simple matter, it is usually worth while to save the "nitron" precipitates and filtrates.

The filtrate and washings are made slightly alkaline with ammonia and the precipitated "nitron" filtered and washed with water. The "nitron" precipitates, along with the asbestos mats collected from the crucibles used in the determinations, are added to dilute ammonia solution and warmed to 60°. The precipitated "nitron" with asbestos is quickly filtered under slight suction and washed with cold water. The mass is then digested in 5% acetic acid until the "nitron" has dissolved, and again filtered. The filtrate is then made slightly alkaline with ammonia and the "nitron" filtered off. It is then washed with cold water and dried in a vacuum. Decomposition may be avoided by conducting the filtering and washing in an atmosphere of inert gas and as much as possible away from light.

Conclusions.

1. The methods employed and the results obtained in this paper by the use of "nitron" clearly show its advantages in the following respects, over other general methods employed for the determination of nitrogen in substances containing it, such as the Dumas, Kjeldahl, and nitrometer methods:

(*a*) Manipulation is simpler.

(*b*) Less time is required.

(*c*) The necessary apparatus is simple and inexpensive.

(*d*) No special skill is required for following directions and obtaining good results.

2. Heretofore "nitron" was used directly as a precipitant in the analysis of nitric acid, perchloric acid, picric acid and their salts. Its use has been extended directly as a precipitant to the analysis of trinitrocresol and its salts, and to mixtures of picric acid and dinitrophenol.

3. "Nitron" has previously been employed to precipitate the nitrate formed on saponification of nitrocellulose. The value of this method has been confirmed in this paper, and the same method is extended for the analyses of the nitric esters of mannite and starch.

4. The failure of the saponification method as applied to nitrocellulose is shown in the case of nitroglycerin, and a modification of the method is developed which is applicable to nitroglycerin.

5. The addition compounds of "nitron" with picric acid and trinitrocresol are shown to be the most insoluble compounds which the trinitrophenols form.

6. The analysis of a mixture of dinitrophenol and picric acid by the use of "nitron" is the simplest method known for such mixtures.

7. By treating true nitrocompounds with a solution of alkaline peroxide it is not possible to convert quantitatively the NO_2 group to the NO_3 group.

FACTORS FOR NITRON DETERMINATIONS.

Substances.	Addition product formed.	Factor for N.	Factor substance sought.
Nitric acid	Nitron nitrate	0.03734	0.16797
NO	Nitron nitrate	0.03734	0.07999
NO_2	Nitron nitrate	0.03734	0.12263
Potassium nitrate	Nitron nitrate	0.03734	0.26946
Sodium nitrate	Nitron nitrate	0.03734	0.22657
Ammonium nitrate	Nitron nitrate	0.03734	0.21335
Guanidine nitrate	Nitron nitrate	0.03734	0.32540
Urea nitrate	Nitron nitrate	0.03734	0.32802
Nitrocellulose	Nitron nitrate	0.03734	(*)
Nitromannite	Nitron nitrate	0.03734	(*)
Nitrostarch	Nitron nitrate	0.03734	(*)
Nitroglycerin	Nitron nitrate	0.03734	(*)
Picric acid	Nitron picrate	0.07765	0.42314
Ammonium picrate	Nitron picrate	0.07765	0.45465
Trinitrocresol	Nitron trinitrocresolate	0.07569	0.43774
Ammonium trinitrocresolate	Nitron trinitrocresolate	0.07569	0.46843
Dinitrophenol	Nitron dinitrophenolate	0.05645	0.37087
Ammonium perchlorate	Nitron perchlorate	...	0.28471
Potassium perchlorate	Nitron perchlorate	...	0.33577
Sodium perchlorate	Nitron perchlorate	...	0.29676

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