The limited solubility of the *p*-hydrazotoluene in absolute alcohol prevented the use of solutions more concentrated than 0.1 molar.

In the manner described for hydrazobenzene, with the above-mentioned modifications, an examination was made of the rate of decomposition of *p*-hydrazotoluene in alcoholic solutions of initial concentration approximately 0.1 and 0.05 molar, respectively.

In conclusion, the author wishes to express his most sincere thanks to Professor Julius Stieglitz, whose fruitful suggestions and inspiring counsel alone have made the successful completion of this investigation possible.

THE QUANTITATIVE SEPARATION OF NITROSUBSTITUTION COMPOUNDS FROM NITROGLYCERIN.[1]

By A. L. Hyde.

Received June 27, 1913.

Introduction.

A practical method for separating nitro compounds from nitroglycerin is of considerable importance in the analysis of explosives. A large number of the explosives now manufactured contain both nitroglycerin and one or more nitro compounds. Though a satisfactory determination of nitroglycerin in such mixtures can often be made with the nitrometer, it has been shown that the nitrometer method is not always available.[2] Moreover, an actual separation of the constituents of an unknown mixture is always more satisfactory than an indirect determination because each of the separated products can be tested.

The method here outlined for separating nitro compounds from nitroglycerin is a further development of a method already described.[3] It overcomes some of the difficulties and increases the accuracy of that method. The method depends upon the differences of solubility of nitroglycerin and nitro compounds in carbon bisulfide and mixtures of acetic acid and water. Nitroglycerin is only slightly soluble in carbon bisulfide but is very soluble in glacial acetic acid and decidedly soluble in mixtures of this acid with water. On the other hand, most nitro compounds though not very soluble in carbon bisulfide are more soluble than nitroglycerin, whereas in mixtures of acetic acid and water they are less soluble than nitroglycerin.

Carbon bisulfide and mixtures of acetic acid and water are only slightly miscible. Hence if a mixture consisting of nitroglycerin and a nitro compound be shaken in a separating flask with carbon bisulfide and an acetic acid and water mixture, allowed to stand, and the two layers be separated,

---

[1] Published by permission of the Director of the U. S. Bureau of Mines.

[2] Storm, C. G., "Effect of the Nitrotoluenes on the Determination of Nitroglycerin by Means of the Nitrometer," *Com. 8th Intern. Congr. Appl. Chem.*, 4, 177.

[3] Hyde, A. L., "Separation of Nitroglycerin from Nitrosubstitution Compounds," *Com. 8th Intern. Congr. Appl. Chem.*, 4, 69.

the nitro compound will be partly separated from the nitroglycerin. The mixture dissolved in the carbon bisulfide layer will be richer in nitro compound and poorer in nitroglycerin than the original mixture, whereas the mixture dissolved in the acetic acid layer will be richer in nitroglycerin and poorer in nitro compound than the original mixture. The separation, however, will be incomplete and experiments have shown that even continued separations of the fractions thus obtained do not give a satisfactory quantitative separation of the two materials. If, however, a continuous fractional separation could be carried on, it is evident that a quantitative separation might be made, though theoretically this could never be complete. To accomplish such a separation, the apparatus here described, which was designed by the writer, is in use in the explosives chemical laboratory of the Bureau of Mines at Pittsburgh.

Description of Apparatus.

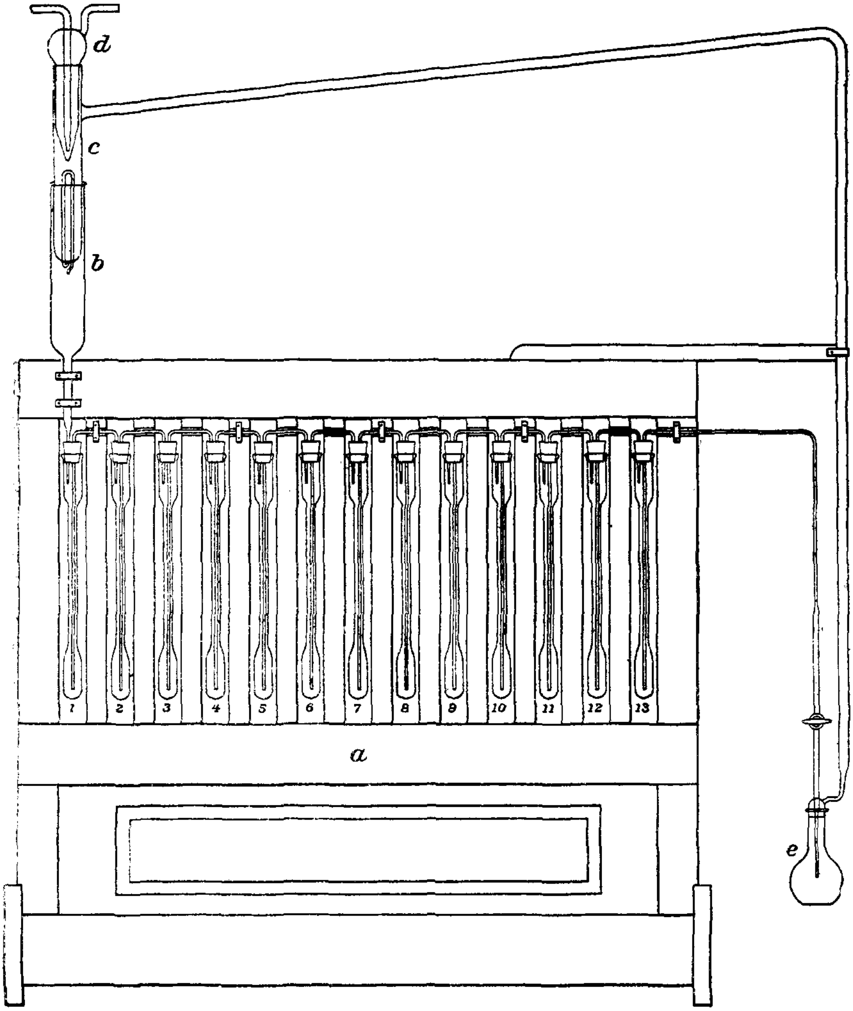
The apparatus consists of a series of 13 tubes for holding the two solvents, a circulating system made of glass tubing, a flask, which may be heated in any convenient manner, at one end of the system, a return pipe from this flask, and a measuring device, condenser, and reservoir at the other end of the system. The whole is mounted in a wooden frame of suitable form and size as shown in the drawing.

The tubes for holding the solvents are made in the form shown. The main shank has an inside diameter slightly less than 1 cm. and a length of about 19 cm. The top and bottom parts have an inside diameter of about 2 cm. The bottom part is about 4 cm. long, the top part about 6 cm. The top of each tube is closed with a No. 3 two-hole rubber stopper.

The circulating system consists of a series of glass tubes of a size to fit snugly the holes of the No. 3 stoppers, and bent at the top in the form of an inverted U. The long arm of each tube is long enough, when passed through the No. 3 stopper and the stopper is tightly inserted in the reaction tube, to reach almost to the bottom of the reaction tube. The short arm, about 6 cm. long, is drawn to capillary size at the end. The long arm of each tube is passed through one hole of a rubber stopper and the short arm through a hole of the stopper next in the series so that the tubes form a continuous chain. A tube leading from the reservoir passes through the first stopper of the series, and a tube leading from the bottom of the last reaction tube to the collecting flask passes through the last stopper.

The bottom of the collecting flask is situated about 30 cm. lower than the bottom of the reaction tubes in order that a syphon may be formed to cause a continuous flow of liquid through the tubes into the flask. Just above the flask is a stopcock designed to regulate the flow through the syphon. The flask has a ground glass stopper with two openings, one of which is connected with the return pipe to the condenser.

The condenser is provided with a syphon measuring device holding 80 cc. for measuring the quantity of solvent that passes through the system. This measuring device empties directly into the reservoir below.



The whole circulating system is fastened in the wooden stand and remains there permanently but the reaction tubes may be removed for cleaning and filling. When the reaction tubes are filled and in place, the whole series forms an air-tight system.

Operation of the Apparatus.

To use the apparatus, tubes 2 to 11, inclusive, are filled up to the bottom of the shank with carbon bisulfide, and the remainder of their length with a mixture of acetic acid and water. About 170 cc. of the mixture are required for the entire apparatus. The mixture should nearly touch the stopper when the tube is placed in the system, thus allowing the capillary point of the U-tube to dip 2 or 3 cm. into the liquid. Tubes 12 and 13 are filled in the same way but with water instead of acetic acid mixture, and are intended to take up any small quantities of acetic acid carried along with the carbon bisulfide from the other tubes. Except for this precaution considerable acetic acid would be carried into the collecting flask and cause delay in subsequent evaporation.

After the solvent tubes are in place, the mixture to be separated is dissolved in 10 to 15 cc. of acetic acid water mixture, and the solution is poured into tube 1 on top of the layer of carbon bisulfide already poured into the bottom part of the tube. When tube No. 1 is in place, carbon bisulfide is poured into the measuring device until it runs over into the reservoir, the collecting flask is put in place and the process is started by opening the cock just above the collecting flask. The rate of flow is regulated by means of the cock so that 3 to 4 cc. of solvent flows into the flask per minute. The flask is heated by immersing it in a dish of hot water, which is heated by a small electric heater.

The action that takes place is as follows: Carbon bisulfide coming down through the tube from the reservoir falls in fine drops through the acetic acid solution containing both nitroglycerin and the nitro compound, extracts some of both and carries this over into tube 2. Here the carbon bisulfide again falls through the acetic acid mixture in a series of fine drops, and most of the nitroglycerin and some of the nitro compound are extracted. The same process is repeated in each reaction tube, the solvent stream being freed more and more from nitroglycerin as it progresses along the system. After a certain quantity of carbon bisulfide has passed through the system, nitro compound entirely free from nitroglycerin begins to appear in the stream flowing into the collecting flask. If sufficient solvent is passed through the system, practically all of the nitro compound will be carried over into the collecting flask. While the solvent is flowing into the collecting flask it is also being evaporated and passed back to the condenser to be used again. After the process is completed, the flask is removed, the solution poured into a small beaker, the solvent evaporated in a bell-jar evaporator as described in *Bulletin* 51[1] and the nitro compound weighed.

In the case of a nitro compound much more soluble in carbon bisulfide than nitroglycerin is, practically all the nitro compound will have passed into the collecting flask before traces of nitroglycerin appear there. In case, however, the difference in solubility is slight, small quantities of nitroglycerin will begin to appear in the collecting flask before all the nitro

---

[1] Snelling, W. O., and Storm, C. G., "The Analysis of Black Powder and Dynamite," Bureau of Mines, *Bull.* 51, 40 (1913).

compound has come over. It is obvious that in these cases a perfectly sharp quantitative separation cannot be made with a single fractionation, but even in these cases, as will be shown, it is possible to obtain satisfactory results with a single fractionation by regulating the quantity of solvent passing through the system.

Some Results of Tests.

The apparatus described above was developed gradually. The first tests were made without a measuring device in the apparatus and several other modifications were made during the progress of the work so that all the results presented in this paper were not obtained under exactly similar conditions. Consequently all the results are not comparable as regards quantity of solvent passing through the system, but they are comparable in a general way and show the degree of accuracy that may be expected from the method.

In using the apparatus there are two factors, the strength of the acetic acid mixture and the quantity of carbon bisulfide passed through the system, that may be varied between rather wide limits. The strength of acetic acid available may be varied from about 70% strength to about 90% strength. If acid less than 70% strength is used, the maximum efficiency of each tube is not obtained, as there is not time for each drop of carbon bisulfide to come to equilibrium with the surrounding liquid during its fall to the bottom of the tube. On the other hand, since pure acetic acid and carbon bisulfide are completely miscible, some water must be present if the apparatus is to operate at all. The practical limit in this direction is about 90% acetic acid to 10% water by volume. The quantity of carbon bisulfide passed through the apparatus may, of course, be varied indefinitely.

In the first tests, the quantity of solvent passed through the system was determined approximately by keeping the rate of flow as nearly constant as possible and noting the time of flow. Pure substances were first used, treated for different lengths of time, and their behavior was determined. The acid mixture used consisted of 70 parts acetic acid (99.5%) pure and 30 parts water, by volume. The following table gives the results of these tests. Columns 3 to 9 show the weight in grams of the substance found in the collecting flask after the apparatus had been in operation for the length of time stated at the head of each column. The percentage of substance recovered is also indicated in these columns. The rate of flow of the solvent into the collecting flask was in all cases approximately $3^1/_2$ cc. per minute.

The results shown in the table seem to indicate that it should be a simple matter to make a practically quantitative separation between most nitro compounds and nitroglycerin. The one exception is crystallin trinitrotoluene, which is so slightly soluble in carbon bisulfide that the amounts

TABLE I.—RESULTS OF SEPARATION TESTS OF PURE SUBSTANCES.

Substances.	Weight. Grams.	Weight of Substance Collected after Distillation for						
		1 hour.	1½ hours.	2 hours.	3 hours.	4 hours.	5 hours.	6 hours.
Trinitrotoluene, melting point 81°–82°	1.485	....	....	....	....	0.875 (58.9%)	1.219 (82.1%)	1.387 (93.4%)
Trinitrotoluene, melting point 81°–82°	0.592	....	....	....	....	....	0.550 (92.8%)	....
Nitroglycerin	4.0	....	....	....	....	0.005 (0.12%)	0.025 (0.6%)	0.075 (1.9%)
Nitroglycerin	2.0	....	....	....	None	0.005 (0.25%)	0.025 (1.2%)	....
Liquid trinitrotoluene	1.656	....	....	1.351 (81.6%)	1.594 (96.3%)	1.626 (98.2%)	....	....
Paranitrotoluene	2.872	2.589 (90.1%)	2.833 (98.6%)	....	....	....	....	....
Dinitrotoluene, melting point 66°–68°	2.308	....	....	1.770 (76.7%)	2.241 (97.0%)	....	....	....
Dinitrobenzene, melting point 81°–82°	1.992	....	....	1.167 (58.1%)	1.828 (91.8%)	....	....	....
Dinitrobenzene, melting point 81°–82°	1.735	....	....	....	....	1.660 (95.70%)	1.694 (97.6%)	....
Nitrobenzene	2.003	1.406 (70.2%)	....	1.933 (96.5%)	....	....	....	....
Mononitronaphthalene	1.975	....	1.920 (97.2%)	1.943 (98.4%)	....	....	....	....
Liquid dinitrotoluene	2.449	....	....	....	2.396 (97.8%)	2.419 (98.7%)	....	...

recovered are considerably less than the amount used. To make a quantitative separation of this substance from nitroglycerin it would probably be necessary to run the apparatus longer and to refractionate the mixture obtained.

The behavior of different compounds when treated alone in the apparatus having been determined in a general way, as shown in the preceding table, experiments were made to determin their behavior when mixed. Several preliminary tests showed that under these conditions their behavior is not quite the same as when they are pure. The solubility of the substances in each other has a retarding effect on the separation, the nitro compounds being held back somewhat by the nitroglycerin and the nitroglycerin being carried over to a small extent by the nitro compounds. With the intent of retarding still more the passage of nitroglycerin, it was decided to use a somewhat stronger acid mixture. Accordingly all further tests were made with mixtures containing 75% acetic acid by volume. It is evident that with a nitro compound whose solubility is only slightly different from that of nitroglycerin the accuracy of the separation depends upon stopping the process after most of the nitro compound has passed over and before much nitroglycerin begins to pass over.

A preliminary test having shown that this point corresponded to the passage of about 1040 cc. of carbon bisulfide through the apparatus, a series of determinations was made with mixtures containing known quantities of nitroglycerin and nitrotoluenes. The process was stopped in

RESULTS OF SEPARATION OF NITRO COMPOUNDS FROM NITROGLYCERIN.

		Composition of mixture.			
		Actual.		By analysis.	
Mixture.	Components.	Grams.	Per cent.	Grams.	Per cent.
1........	Nitroglycerin	1.967	50.7	1.964	50.6
	Liquid trinitrotoluene	1.910	49.3	1.913	49.4
2........	Nitroglycerin	2.500	74.7	2.543	75.6
	Liquid trinitrotoluene	0.848	25.3	0.805	24.4
3........	Nitroglycerin	2.414	44.8	2.369	44.0
	Liquid dinitrotoluene	2.972	55.2	3.017	56.0
4........	Nitroglycerin	2.810	57.1	2.869	58.3
	Liquid trinitrotoluene	2.114	42.9	2.055	41.7
5........	Nitroglycerin	2.315	54.5	2.327	54.8
	"Lydol"(*a*)	1.931	45.5	1.919	45.2
6........	Nitroglycerin	2.146	41.7	2.125	41.3
	Liquid dinitrotoluene	3.007	58.3	3.028	58.7
7........	Nitroglycerin	2.717	76.9	2.698	76.4
	Liquid trinitrotoluene	0.816	23.1	0.835	23.6
8........	Nitroglycerin	3.323	76.3	3.308	76.0
	Liquid dinitrotoluene	1.032	23.7	1.047	24.0

(*a*) A trade name for a commercial liquid nitro product.

each case after approximately 1040 cc. of solvent had passed through the apparatus, and the contents of the collecting flask which was assumed to be nitro compound was then weighed. The assumption was not exactly true, since a small quantity of nitroglycerin was undoubtedly present in the nitro compound finally weighed in each case, but the error thus introduced was not large.

Below are shown the actual compositions of the mixtures and the compositions determined.

A slight modification was made in the apparatus after the above mixtures had been tested. With this modification it was found that the passage of about 880 cc. of solvent through the apparatus sufficed to carry over practically all the nitro compound. Three mixtures were tested using this quantity of solvent. The results are noted below:

RESULTS OF SEPARATION WITH MODIFIED APPARATUS.

		Composition of mixture.			
		Actual.		By analysis.	
Mixture.	Components.	Grams.	Per cent.	Grams.	Per cent.
1	Nitroglycerin	2.623	52.7	2.595	52.2
	Liquid trinitrotoluene	2.353	47.3	2.381	47.8
2	Nitroglycerin	2.838	63.5	2.831	63.4
	Liquid trinitrotoluene	1.631	36.5	1.638	36.6
3	Nitroglycerin	3.400	78.1	3.406	78.2
	Liquid trinitrotoluene	0.955	21.9	0.949	21.8

In order to determin whether any nitroglycerin was present in the product obtained in the collecting flask, tests were made in several of the foregoing experiments. These tests showed that in no case was the separation entirely complete, but that 1 to 2% of the quantity of nitroglycerin originally present had passed into the collecting flask. However, as the above results show, the accuracy is sufficient for most purposes. If in any particular case it is desired to obtain the nitro compound more nearly free from nitroglycerin than can be obtained with one separation, a second free separation may be made, which will still further reduce the proportion of nitroglycerin. But this is a rather tedious process and usually should not be necessary. A double separation of one mixture was made to determin what accuracy could be expected.

The mixture contained 3.475 grams, or 58.8% of nitroglycerin, and 2.434 grams, or 41.2% of liquid trinitrotoluene. The nitrotoluene obtained after two separations weighed 2.388 grams, or 40.4% of the original mixture. A test of the nitrotoluene separated showed that it contained less than 10 mg. of nitroglycerin.

Separation of Nitro Compounds from Each Other.

Inspection of the table on page 1178 shows that there is a marked difference in the time required to recover the nitro compound, depending upon whether it is a mono-, di-, or trinitrotoluene compound. This suggested the possibility of separating these different compounds from each other. Some preliminary tests were made with the three different nitrotoluenes to determin if such a separation were possible. Acid of 85% strength was used. It was found that after 320 cc. of solvent had passed into the collecting flask nearly all of the mononitrotoluene was there.

The same quantity of solvent carried over 20 to 30% of the dinitrotoluene and only slight traces of the trinitrotoluene, whereas 640 cc. of solvent carried over almost all of the dinitrotoluene and from 20 to 30% of the trinitrotoluene.

It is evident from the tests that a separation of mononitrotoluene from dinitrotoluene or of dinitrotoluene from trinitrotoluene is not possible with a single treatment, but an almost complete separation of the mono compound from the tri compound is possible. This latter possibility may occasionally have a practical application. For instance, the ether extract from a certain English coal-mining explosive consists of a mixture of trinitrotoluene and mononitronaphthalene. Obviously, a direct separation of these two materials is to be preferred to an indirect determination, such as the nitrogen determination by the Kjeldahl method. Separation of a mixture of known composition of these materials gave the following results:

RESULT OF SEPARATION OF A MIXTURE OF MONONITRONAPHTHALENE AND TRINITROTOLUENE.

	Composition of mixture.	
Component.	Actual. Per cent.	By analysis. Per cent.
Mononitronaphthalene	44.0	43.1
Trinitrotoluene	56.0	56.9

Although the analysis of a mixture containing all three nitrotoluenes is not possible by a single separation, it appears that it might be possible by several fractionations. This method was tried and the results given below obtained. The procedure used was to refractionate twice the portions found in the collecting flask after 320 cc. and 640 cc. of solvent had passed into the collecting flask. This should give a mononitrotoluene containing not more than 1 or 2% of the dinitro compound and dinitrotoluene containing about the same percentage of the trinitro compound. A mixture of mononitrotoluene and dinitrotoluene treated in this way gave the following result:

SEPARATION OF MONONITROTOLUENE AND DINITROTOLUENE.

	Composition of mixture.			
	Actual.		By analysis.	
Component.	Grams.	Per cent.	Grams.	Per cent.
Mononitrotoluene	1.327	25.0	1.369	25.8
Dinitrotoluene	3.974	75.0	3.932	74.2

A mixture of all three nitrotoluenes gave the results shown below:

Separation of Mono-, Di-, and Trinitrotoluene.

	Composition of mixture.			
	Actual.		By analysis.	
	Grams.	Per cent.	Grams.	Per cent.
Mononitrotoluene	1.731	22.0	1.761	22.4
Dinitrotoluene	4.175	53.1	4.047	51.5
Trinitrotoluene	1.952	24.9	2.050	26.1

Some further tests made upon commercial liquid nitrotoluenes seemed to indicate that the solvent action of the different constituents interfered with this separation and that results obtained upon these substances were not nearly as accurate as the above results would seem to indicate. This point is being further investigated.

Conclusions.

The foregoing results show that, by means of the method outlined, an almost quantitative separation may be made between all nitro compounds tested, and presumably any nitro compound, and nitroglycerin. In the case of most nitro compounds, the separation after a single treatment is complete enough for most practical purposes. Greater purity of product, if necessary, may be obtained by a second fractionation. Mononitro compounds may be separated from trinitro compounds in fairly pure condition by a single fractionation.

Separation of nitro compounds from each other in fairly pure condition may, perhaps, be obtained by several fractionations but satisfactory results along this line have not yet been obtained.

Attention should also be called to the fact that this is a general method and might perhaps find useful application in other fields than that for which it was devised. By its means, differences of solubility may be used to obtain separations in much the same way that differences in boiling points are used in fractional distillations.

The necessary conditions that the method may be available in any particular case are as follows:

1. Two nearly immiscible solvents must be found, one of which should have a considerably higher specific gravity than the other as well as a fairly low boiling point; (2) considerable differences of solubility of the constituents of the mixture to be separated in these two solvents are necessary; (3) the substance carried over into the collecting flask must not be so volatil that the solvent can not be separated from it by evaporation.

If these conditions can be satisfied it would seem that the method might be used to advantage, especially in case no other method is available.

Acknowledgments are due the members of the explosives chemical laboratory of the Bureau of Mines, for helpful suggestions during the progress of this work.