The Quantitative Separation of Nitro-body Mixtures from Nitroglycerin.

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IN the process of explosives' analysis it is frequently necessary to separate nitro-body mixtures from nitroglycerin, as these substances are taken out together in the ether extract.

As stated by Snelling and Storm in their booklet on the *Analysis of Black Powder and Dynamite*, published by the U.S. Bureau of Standards, p. 62, there is no satisfactory method generally available for the purpose indicated. The analysis of such mixtures is usually made by estimating the nitroglycerin by means of the nitrometer and finding the amount of nitro-body mixture by difference. An approximate estimation of the nitro-body can also be made by destruction of the nitroglycerin by treatment with a hydrochloric acid solution of ferrous chloride by heating on the water bath, and recovery of the nitro-body by extraction with ether.

During the progress of work involving the titration of nitroglycerin by means of ferrous sulphate, according to the well-known method for the titration of nitric acid (Bowman and Scott, *J. Ind. Eng. Chem.*, 1915, **7**, 766; *Chem. News*, 1916, **114**, 2957; Scott's *Text-Book of Analysis*), it was considered that if this method were applied to a mixture of nitroglycerin and nitro-body, the nitro-body could be recovered from the reaction mixture by extraction with ether. It was thought that probably the results would be too high, owing to a further nitration of the nitro-body during the destruction of the nitroglycerin. Such was, indeed, found to be the case, particularly with mononitrotoluene. A commercial mixture of dinitrotoluene, trinitrotoluene and dinitrobenzene did not appear to be so sensitive to the nitrating action. The first experiments with such a mixture gave excellent results, but it was considered that, as the nitro-body was more or less impure, the results might be due to a compensation of errors—further nitration on the one hand, and loss of impurity by the action of strong sulphuric acid on the other.

In subsequent experiments, therefore, the nitro-body mixture was first purified by dissolving a quantity in concentrated sulphuric acid, and pouring the solution into water. The dilute solution was then extracted with ether, the ethereal solution dried over calcium chloride and distilled, and the residue dried to constant weight *in vacuo*.

In the experiments with mononitrotoluene it was evident that nitration to dinitrotoluene was taking place.

Information was received privately from the United States that methyl alcohol was added to reaction mixtures in which nitroglycerin was being destroyed, for

the purpose of preventing further nitration of the nitro-body. Varying quantities of methyl alcohol were therefore added, in order that this substance might be acted on by the nitric acid liberated from the nitroglycerin in preference to the nitro-body. Very satisfactory results were obtained in this way. The following table shows the results obtained up to this stage of the investigation:—

TABLE 1.

Estimation of Nitro-body in presence of Nitroglycerin in Synthetic Mixtures of the two by treatment with ferrous sulphate and recovery of the Nitro-body by extraction with ether. Nitroglycerine present .8—1.4 grams.

	Nitro-body Taken Grm.	Nitro-body Found Grm.
Commercial nitro-body mixture. (before purification)	0.332	0.336
“ “	0.478	0.472
Mononitrotoluene (distilled).	0.31 (calculated to D.N.T. 0.412 grm.)	0.412
“ “ “	0.253 (calculated to D.N.T. 0.340 grm.)	0.338
Mononitrotoluene (distilled) reac- tion conducted in presence of 20 c.c. methyl alcohol.	0.1233	0.145 Partially solid, showing presence of D.N.T.
“ “ “	0.2024	0.193 liquid.
Mononitrotoluene (distilled) reac- tion conducted in presence of 40 c.c. methyl alcohol.	0.199	0.205
“ “ “	0.161	0.167
Commercial nitro-body mixture after purification. Reaction	0.238	0.238
conducted in presence of 40 c.c. methyl alcohol.	0.486 0.314 0.162	0.482 0.307 0.161

The results given in the above table represent various ratios of nitroglycerin to nitro-body, and it is evident that the results are independent of this ratio. This is not the case when the determination is carried out by means of the nitrometer. It will be seen that, while it is necessary to have 40 c.c. of methyl alcohol present during the reaction in the case of mononitrotoluene, it is not so clear that this is necessary in the case of commercial nitro-body mixture, which is probably less easily nitrated. As the manipulation with 40 c.c. of methyl alcohol is more tedious than with 20 c.c., owing to the heat generated on the addition of sulphuric acid (it being necessary to keep the temperature of the reaction mixture below 20° C.

to avoid possible further nitration), it was decided to carry out a series of experiments using 20 c.c. of methyl alcohol. Table 2 shows the results obtained:—

TABLE 2.

Estimation of commercial Nitro-body Mixture in presence of Nitroglycerin by means of Ferrous Sulphate. Synthetic Mixtures.

	Commercial Nitro-body Mixture Taken Grm.	Nitro-body Found Grm.
Reaction conducted in presence of	0.408	0.406
20 c.c. methyl alcohol.	0.097	0.101
	0.133	0.137

These results having proved satisfactory, and the first result in Table 1 also being satisfactory, it was thought that, perhaps, with the commercial nitro-body mixture, methyl alcohol might be unnecessary. Table 3 shows the results obtained:—

TABLE 3.

Estimation of commercial Nitro-body Mixture in presence of Nitroglycerin by means of Ferrous Sulphate.

	Commercial Nitro-body Mixture Taken Grm.	Nitro-body Found Grm.
Reaction conducted in absence of	0.094	0.1650 } Partly
methyl alcohol.	0.065	0.1138 } solid.
“ “ “	0.063	0.150 } Completely
“ “ “	0.066	0.148 } solid.

High results and solidification showed that further nitration was taking place, and that therefore methyl alcohol was necessary.

The question of the drying of the residue of nitro-body after the evaporation of the ether was rather difficult. Occasionally, high results were obtained which could not be attributed to further nitration of the nitro-body. At other times, low results were obtained after prolonged drying, and this was attributed to volatilisation of the nitro-body *in vacuo*. In the first place it was considered that thorough drying of the ethereal solution over calcium chloride was most necessary, because, otherwise, when the ether evaporated off, it left an emulsion of nitro-body and water, which took a very long time to dry *in vacuo*, and the substance could never be said to attain constant weight. Drying at ordinary pressure over sulphuric acid was satisfactory, but very slow; some residues took as long as 90 hours to become constant in weight.

In order to determine the best conditions for drying nitro-body residues, weighed quantities of the purified nitro-body were dissolved in ether, and the ether was removed in different ways:—

(1) Spontaneous evaporation of the ether, after thorough drying of the ethereal solution over calcium chloride, and drying the residue, either over sulphuric acid

at ordinary pressures for a prolonged period or *in vacuo* for 24 hours. This method showed a loss of less than 0.5 per cent.

(2) The ether was evaporated off quickly over a water bath, and the residue dried on the bath, either with or without the addition of a little alcohol. Losses by this method amounted to 1 to 2 per cent. Spontaneous evaporation of the ether and drying *in vacuo* over sulphuric acid was therefore adopted. The following table shows the results obtained:—

TABLE 4.

Separation of commercial Nitro-body from admixture with Nitroglycerin by the Ferrous Sulphate method.

Series	Nitro-body Taken Grm.	Nitro-body Found Grm.	Remarks
1.	0.0948	0.0932	Ether evaporated off in presence of CaCl_2 . Residue dried at atmospheric pressure.
	0.1408	0.1400	
	0.1090	0.1066	
	0.1668	0.1726	
2.	0.1706	0.1600	Ether solution not dried sufficiently over CaCl_2 . Residue dried <i>in vacuo</i> .
	0.1614	0.1502	
3.	0.1276	0.1272	Ethereal solution dried over CaCl_2 for 24 hours. Evaporated spontaneously and dried <i>in vacuo</i> for 24 hours.
	0.1354	0.1354	
	0.1424	0.1476	
	0.1927	0.1899	
	0.1312	0.1313	
	0.2363	0.2437	
	0.1988	0.2021	
	0.1751	0.1705	
	0.1944	0.1957	
	0.2530	0.2507	
	0.2722	0.2664	
	0.2592	0.2623	

It will be seen that in series 3, where the conditions of drying were satisfactory, the results are all within 3 per cent. of the truth. This degree of accuracy is perfectly satisfactory from the point of view of the examination of explosives for manufacturing control, where the nitro-body does not usually amount to more than one or two per cent.

Experience gained in the recovery of less volatile substances than nitro-body mixtures from admixture with nitroglycerin, by the ferrous chloride method mentioned at the beginning of the paper, showed that good results could be obtained with such substances. This fact suggested the possibility of conducting the ferrous chloride separation in the cold, to prevent loss of nitro-body, and in the presence of methyl alcohol, in order to prevent further nitration of the nitro-body, as previously

explained. The results obtained were quite as good as those obtained by the ferrous sulphate method, as is shown in the following table:—

TABLE 5.

Separation of Nitroglycerin from Commercial Nitro-body Mixture by modified Ferrous Chloride Method.

Nitro-body Taken Grm.	Nitro-body Found Grm.
0.5286	0.5367
0.1756	0.1786
0.2589	0.2606
0.3170	0.3260
0.3458	0.3508
0.2692	0.2750
0.3452	0.3524

The manipulation with the ferrous chloride method is more satisfactory, owing to the fact that the concentration of the acid does not need to be so great, and, consequently, no great dilution of the reaction mixture is required before ether extraction. On the other hand, the ferrous sulphate method has an advantage, in that the end point indicating the complete destruction of the nitroglycerin is definite, whilst the completion of the reaction with ferrous chloride can only be ensured by adhering to the conditions found to be satisfactory by working with synthetic mixtures. Both the ferrous sulphate and the ferrous chloride methods have been applied to the analysis of actual explosives with satisfactory results. Of the two methods dealt with, the ferrous chloride one has been found most satisfactory from the manipulative point of view, and has, therefore, been adopted by the authors. The method is carried out as follows:—

The ethereal solution of nitroglycerin and nitro-body, obtained on extracting an explosive with pure dry ether, is allowed to evaporate spontaneously. The residue is dissolved in 40 c.c. of methyl alcohol, and 25 c.c. of saturated ferrous chloride solution added for every gram. of nitroglycerin present in the quantity of explosive taken. An addition of 25 c.c. of concentrated hydrochloric acid is also made.

The solution is set aside at room temperature for at least 24 hours, and then extracted with three quantities of ether, 50 c.c. at a time.

The ether extracts are united, washed repeatedly with 50 c.c. of water, until free from iron salts, and dried by introducing a quantity of granular calcium chloride into the separating funnel. The ether solution is filtered into a large crystallising basin, the calcium chloride and the funnel are thoroughly washed with pure dry ether, and the washings filtered into the same basin. The filter is also washed with dry ether, and the whole filtrate and washings allowed to evaporate spontaneously. The residue is washed from the basin into a weighed fat-extraction flask by means of a little pure dry ether, the ether is allowed to evaporate spontaneously, and the flask and residue finally dried to constant weight *in vacuo* over

sulphuric acid. The fat-extraction flask is much more convenient for drying and weighing than the large basin.

When the explosive contains substances, like wood-meal, which yield extracts to ether, a suitable correction must be deducted from the nitro-body as estimated before calculating the percentage on the explosive, because the extract from the wood-meal will not be touched by ferrous chloride solution, and will appear in the final ether extract together with the nitro-body.

The authors desire to express their thanks to the research committee of Messrs. Nobels Explosive Co., Ltd., for permission to publish these results, and to Mr. Rintoul for his interest during the progress of the work.

DISCUSSION.

Mr. DUPRÉ said the method brought forward by the authors should prove of value, older methods having always been unsatisfactory and the results unreliable owing to the further nitration of the mono- and dinitro-bodies. From the figures given, it certainly seemed that this method gave remarkable results, far more accurate than it was possible to get by older methods, and the manipulation seemed so simple that he did not consider any criticism to be required. Referring to the drying of the nitro-bodies, he stated that one frequently came across substances which, on drying, reached a stage where the remaining moisture was so enclosed by the exterior dried portions that very prolonged exposure to heat or drying agents was required to drive it off. In such cases he had found it useful to mix it, previous to drying, with some inert material such as French chalk, so as greatly to increase the surface exposed. However, he did not consider that anyone could complain of only 24 hours' drying.