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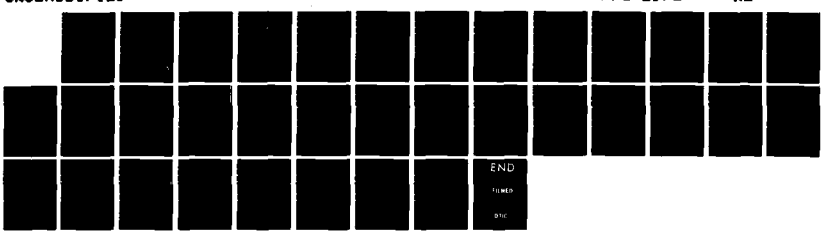

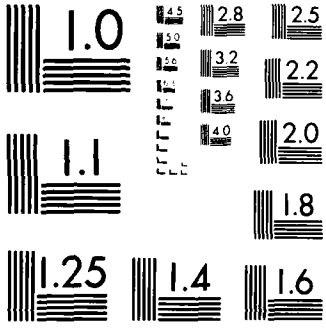

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AUSTRALIA

DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

WEAPONS SYSTEMS RESEARCH LABORATORY

DEFENCE RESEARCH CENTRE SALISBURY
SOUTH AUSTRALIA

TECHNICAL MEMORANDUM

WSRL-0368-TM

THE DETERMINATION OF DINITROTOLUENE IN SINGLE BASE PROPELLANTS

M. MULAR

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DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

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TECHNICAL MEMORANDUM

WSRL-0368-TM

THE DETERMINATION OF DINITROTOLUENE IN SINGLE BASE PROPELLANTS

M. Mular

SUMMARY

Six single base gun propellants of three different types (AR 2206, NH and FNH) were analysed for dinitrotoluene by three different methods, viz titanous chloride reduction, gas chromatography and high performance liquid chromatography (HPLC). In general, similar results were obtained by all three methods.

Although any of the three methods can be used for the determination of dinitrotoluene, the HPLC method is recommended - the equipment is automated and microprocessor controlled, and analyses can be performed relatively quickly, with good precision and with the lowest relative standard deviation of the order of 0.3%. It is recommended that the HPLC method be adopted as a standard test method.

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1. INTRODUCTION

Dinitrotoluene (DNT) is an organic compound which may be incorporated in single base gun propellants either as an ingredient (eg in NH and FNH propellants) or as a deterrent coating in small arms propellants (eg AR 220b).

For many years the British and USA test method for the determination of DNT in single base propellants has been based on the use of titanous chloride ($TiCl_3$)(ref.1,2). Both test methods are very similar with the main difference being that in the USA method acetic acid is used whereas in the British method diethyl ether is used for the extraction of the propellant. In both methods the propellant extract is treated with an excess of $TiCl_3$, followed by the titration with ferric ammonium sulphate solution. The British method was generally used at the Materials Research Laboratories (MRL) and its use has continued at the Weapons Systems Research Laboratory (WSRL) since the transfer of gun propellant research and development activities from MRL to WSRL in 1977.

The $TiCl_3$ method, however, has some drawbacks - it is tedious time-consuming and involves the preparation and standardisation of several reagents, including titanous chloride solution which is unstable and readily oxidises in air.

The desirability of introducing a more modern instrumental test method which would be faster and more convenient became apparent. Recent literature reports have described the use of high performance liquid chromatographic (HPLC) and gas-liquid chromatographic (GLC) techniques for the determination of DNT and other ingredients in propellant formulations(ref.3-5). In the last few years the introduction of GLC and HPLC methods for the determination of a variety of propellant ingredients has appeared in the USA (MIL-STD 286) and British (MQAD) test methods(ref.6-9).

Currently, in Australia the Explosives, Ammunition and Pyrotechnics (EA&P) subcommittee of the Defence Standardisation Committee has draft test methods for propellants which include the $TiCl_3$ method(ref.10) (based on the British method, reference 1) and a GLC method for determination of DNT recently submitted by the Mulwala Explosives Factory (MEF)(ref.11).

A GLC method for determination of DNT was developed in this Laboratory before the MEF draft method was submitted to the EA&P subcommittee, and is described in detail in this report - both WSRL and MEF methods are however very similar. In addition to the GLC method being developed, the recent acquisition by this Laboratory of a liquid chromatograph prompted an investigation into the use of HPLC for the separation and determination of DNT in propellant extracts.

This report describes the $TiCl_3$ method and the development of the GLC and HPLC methods for the determination of DNT in single base propellants. The objective of this report is to compare the modern, instrumental analytical methods with the classical technique currently in use, with the aim of replacing the old $TiCl_3$ method with one which will give results as reliable as the existing method, but which is faster and easier to carry out, thereby increasing the (cost) efficiency of the analysis.

2. DESCRIPTION OF METHODS

In this work, six single base gun propellants, viz types NH (two lots), FNH (two lots), and AR 2206 (two lots), were analysed for DNT content by three different methods (1) titanous chloride reduction (2) GLC and (3) HPLC. A brief description of each method is given below and full details are given in Appendices I, II and III. The NH and FNH propellants were ground so that all the material passed through a 2 mm sieve. The AR 2206 propellants, however, being small grained were not ground or sieved. The propellants were extracted with boiling dichloromethane in a Soxhlet apparatus over a water bath for 70 hours - extraction beyond this time showed (by GLC) that no further DNT was extracted. (The extraction time depends on the nature of the propellant and the degree of grinding. For some types of propellant, 70 hours extraction time may not be necessary - the extraction time should be checked for new propellant types). The propellant extract was then analysed by the three methods as described below.

2.1 Titanous chloride method

The dichloromethane propellant extract was evaporated and the residue made up in ethanol. An aliquot of the ethanolic solution was then heated with an excess of titanous chloride solution under nitrogen. The reduction of the nitro group proceeds as shown in the following equation:

$$R\text{-}NO_2 + 6Ti^{+++} + 6H^{+} \rightarrow RNH_2 + 6Ti^{++++} + 2H_2O$$

The solution was cooled and titrated with ferric ammonium sulphate solution using ammonium thiocyanate as indicator. The ferric ammonium sulphate solution was standardised by reduction with zinc amalgam, followed by titration with potassium dichromate. All the results obtained for propellant samples (listed in Table 1) have been corrected for added ingredients. See Appendix I for full details of this method.

2.2 Gas chromatrography method

An aliquot of internal standard solution (methyl centralite) was added to the dichloromethane propellant extract and the mixture was injected on to a stainless steel column 2 m x 3 mm OD packed with 3% OV-101 (silicone) on Chromosorb W HP 100-120 mesh. The gas chromatograph was equipped with a flame ionisation detector (FID) and an electronic integrator. Temperature programming enabled the separation of the isomers 2,6- and 2,4-DNT and other ingredients which had been extracted including diphenylamine (DPA) and dibutyl phthalate (DBP). (DPA and DBP are ingredients in NH and FNH propellants; AR 2206 also contains DPA but not DBP.) Peaks areas were measured using the integrator, and the linearity of the FID response was checked by injecting a series of five DNT standard solutions of increasing strength (0.16, 0.24, 0.32, 0.40 and 0.48%) spanning the range expected in the final propellant extracts. (The specification level of DNT in NH, FNH propellants is 10 ± 1%, and in AR 2206 4-8%). See Appendix II for full details of this method.

2.3 High performance liquid chromatography method

An aliquot of internal solution (p-nitrotoluene, PNT) was added to the dichloromethane propellant extract and the mixture was injected on to a silica column (250 mm x 4 mm ID, Si 10 µm). The liquid chromatograph was microprocessor controlled and was equipped with a UV detector operating at 254 nm. Solvent gradient programming using a mixture of dichloromethane and cyclohexane enabled the separation of PNT, 2,6- and 2,4-DNT,

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diphenylamine and dibutyl phthalate. Peak areas were printed. The linearity of the UV detector response was checked by injecting a series of DNT standard solutions of increasing strength (0.16, 0.24, 0.32 and 0.40% solutions). See Appendix III for full details of this method.

3. RESULTS AND DISCUSSION

The results obtained on the analysis of six single base gun propellants (two lots each of types NH, FNH and AR 2206) by three methods (1) titanous chloride reduction (2) GLC and (3) HPLC are given in Table 1. For each method, a separate weighing and extraction of the propellant was carried out - the extract was then analysed at least twice, up to a maximum of eight determinations. For example, three separately weighed portions of propellant number 1 (NH 033, MEM 1913) were extracted - one extract was analysed four times by the $TiCl_3$ method, the second extract was injected three times on to the gas chromatograph, and the third extract was injected eight times on to the liquid chromatograph. There was no significant reason for carrying out different numbers of determinations for the three methods. However, for two propellant samples (number 2, high DNT content and 6, low DNT content) eight determinations were carried out by each of the three methods in order to provide more meaningful statistics. All the results obtained for the propellant samples have been corrected for added ingredients - refer to Appendix I.

The accuracy of all three methods was checked by carrying out controls using accurately prepared solutions of pure DNT - these solutions were then treated in the same way as a propellant extract. Ideally, the values obtained for the control should be 100% - values less than this arise from unavoidable experimental errors in weighing and pipetting, and in the case of the $TiCl_3$ method in judging colour changes and impurities in the sample. The average of control values obtained by the three methods were all close to 99% which is considered to be excellent ie all three methods are very acceptable.

It is evident from the experimental work (described in the Appendix I) that the titanous chloride method is tedious and time-consuming. Because of the ready oxidation of $TiCl_3$ in air, the $TiCl_3$ solution has to be kept in a tightly stoppered bottle and standardised before use. The $TiCl_3$ method also has the disadvantage that no distinction can be made between the isomers 2,6- and 2,4-DNT or other nitro components which may be present.

Although an OV-101 column provided good separation of DNT in the GLC method, the use of different columns eg OV-17(ref.5) and UC-W98(ref.6,11) and different internal standards in the GLC determinations of DNT have been reported, and similar separations were obtained. A typical gas chromatogram of an NH propellant extract is shown in figure 1. Note that although only the 2,6- and 2,4-DNT were quantitatively measured in this chromatogram, diphenylamine and dibutyl phthalate could also be determined if required. The duration of a typical chromatographic run was about 10 min. The peak areas were measured with an electronic integrator. A mixture of equal amounts of 2,6- and 2,4-DNT in solution, when chromatographed, gave identical response on the FID for the two isomers, allowing for simple summation of the areas of the two isomers to obtain total DNT. This equal response by the flame ionisation detector for the two isomers is expected, since the FID responds to the number of carbon atoms per molecule, which in the case of isomers, is identical.

The linearity of the response of the FID was checked by preparing and injecting five DNT standard solutions of increasing strength (0.16, 0.24, 0.32, 0.40 and 0.48% solutions). These solutions cover the range of DNT

concentrations likely to be found in gun propellant extracts. The FID response was linear over this range. Figure 2 shows a straight line plot of area DNT/area int. STD versus concentration for the five solutions (A, B, C, D and E).

In the gas chromatograms of gun propellants (figure 1), the ratio of 2,4- to 2,6-DNT was 94:6. This ratio was constant for all the six propellants studied in this work. The standard solutions of DNT and methyl centralite (int. STD) in dichloromethane were stable for at least six months, unlike $TiCl_3$ solution which was standardised prior to use.

In the HPLC method, the dichloromethane propellant extract was injected on to a silica column fitted to a Spectra-Physics 8000A liquid chromatograph. A mobile phase mixture of two solvents, dichloromethane and cyclohexane, in the proportions shown in Table 3 was used in a linear gradient program which enabled the separation of the internal standard (PNT), the isomers 2,6- and 2,4-DNT as well as other ingredients (diphenylamine and dibutylphthalate). The order of elution of 2,6- and 2,4-DNT, diphenylamine and dibutylphthalate were the same by both HPLC and GLC. Other separations of DNT by HPLC have been reported using reverse phase C-18 and cyano-sil-x-1 columns(ref.7).

A typical HPLC chromatogram is shown in figure 3. Note that in most cases the printer was stopped just after elution of the 2,4-DNT - consequently, no diphenylamine or dibutylphthalate peaks are seen in figure 3 - the flow of the mobile phase (composition in Table 3), however, was continued for sufficient time to ensure that these components were eluted from the column. Although the diphenylamine and dibutylphthalate were not determined in this work, the method is very suitable for such determinations if required.

An SP8400 UV detector operating at 254 nm was used to detect the eluted constituents of a mixture. A mixture of equal amounts of 2,6- and 2,4-DNT did not give identical response on the UV detector. At 254 nm, the extinction coefficient of 2,6-DNT is less than that of 2,4-DNT, due to the relative steric crowding of 2,6-DNT which hinders the coplanarity of the nitro group with the benzene ring, thus lessening the extent of π-electron delocalisation. The response of the 2,6-DNT was only 38% that of the 2,4-DNT. In this case, a calibration standard solution contained accurately measured amounts of both 2,6- and 2,4-DNT.

The linearity of the response of the UV detector was checked by preparing and injecting four standard solutions of 2,4-DNT in dichloromethane of increasing strength (0.16, 0.24, 0.32 and 0.40%). These solutions cover the range of DNT concentrations found in the gun propellant extracts. The UV detector response showed slight deviation (5%) from linearity at the high concentration end of the graph - see figure 4. This may be due to overloading of the column, or, more probably, the detector. Consequently, the calculations of %DNT in samples was determined by comparison with standards of equivalent concentration.

The HPLC method is relatively fast and easy and has a microprocessor keyboard control which enables the generation of linear or gradient binary or ternary solvent mixtures, multiple sample analysis (in this case six), multiple injections per sample (eight), a printout of the chromatogram and retention times, and provides statistical data as well. Another advantage is that the operator is free to carry out other duties during a microprocessor-controller run.

Table 2 lists the means, standard deviation and relative standard deviation (RSD %) obtained by the three methods for six propellant samples. In all cases the RSD obtained by the HPLC method (about 0.26%) was lower than that

obtained by the other two methods. The GLC method had the highest RSD (1.5%) and this is thought to be mainly due to instrument instability, bearing in mind that the gas chromatograph and integrator are about 20 years old. Considerable difficulty was experienced on some occasions in obtaining reproducible results from the gas chromatograph. Better reproducibility (better than 1% RSD) would be expected from a more modern (microprocessor-controlled) gas chromatograph which would have better stability in electronics and temperature control. The low RSD of the HPLC method is no doubt a result of stable electronics, microprocessor-control and the use of a constant volume (10 µL) injection loop for the introduction of the sample.

From Table 2, it can be seen that all three methods give similar results, with the $TiCl_3$ and HPLC results being in very close agreement. For practical purposes there is no significant difference between any of the three methods because the propellant specification limits are quite wide ie for NH, FNH propellants the specification for DNT content is 10 ± 1%, and for AR 2206 ~~a~~ DNT. Consequently, all three methods are suitable for specification testing of propellants. Further statistical treatment of the results is given in Appendix IV.

In terms of sensitivity and selectivity, both GLC and HPLC methods are superior to the $TiCl_3$ method. The chromatographic methods are also free from possible interferences due to the presence of other propellant ingredients in the extract since these are well separated from the DNT peaks. In terms of speed and ease of use, the $TiCl_3$ method is certainly the slowest and most tedious method - the GLC and HPLC methods are comparable. All three methods give similar accuracy (based on controls) and reliability, but the best reproducibility is obtained from the HPLC method.

4. CONCLUSION

In general, similar results were obtained by the $TiCl_3$, GLC and HPLC methods for the determination of %DNT in single base gun propellants. The GLC and HPLC methods are, however, faster and easier to carry out, and either method would be an acceptable replacement method for the $TiCl_3$ method. The HPLC method is the most favoured method - it is fast, convenient and gives the most reproducible results.

5. ACKNOWLEDGEMENT

The help is acknowledged of Mrs A. Scarratt for operating the HPLC.

REFERENCES

No.	Author	Title
1	-	"The Examination of NH and FNH smokeless Cannon Powders". The Director of Materials Quality Assurance Ministry of Defence, London, England (formerly Chemical Inspectorate), Method EA9, 25 November 1952
2	-	"Propellants, Solid : Sampling, Examination and Testing". Department of Defense, MIL-STD-286B, Washington DC. USA Method 205.1.2, 1 December 1967
3	Juhasz, A. and Doali, J.O.	"High Performance Liquid Chromatographic Analysis of Propellants". ICT Jahrestagung, 1977, 22-24 June, p. 161
4	Paterson-Jones, J.C. and McAuley, C.D.	"A Comparison of Three Column Types in the Analysis of Some Propellants by High Speed Liquid Chromatography". ICT Jahrestagung, 1977, 22-24 June, p. 63
5	Kelso, A.G.	"The Analysis of Single-Base Propellant Compositions Using Gas Liquid Chromatography". MRL Tech Note 358, November 1974
6	-	"Dinitrotoluene, Stabilizers and Plasticizers". MIL-STD-286B, Washington DC. Method 226.2, 1 September 1980
7	-	"Nitroglycerine, 2,4-Dinitrotoluene, Diphenylamine and Dibutylphthalate". Ibid Method 208.5.1, 1 September 1980
8	-	Reference 1, Method VPC 5
9	-	Reference 1, Method M3/77
10	-	Australian Defence Standard, Methods of Test for Propellants, Draft No.3, August 1981, Method 8/2
11	-	Ibid Method 10/2
12	Alder, H.L. and Roessler, E.B.	"Introduction to Probability and Statistics". 4th ed. 1968, W.H. Freeman and Co., San Francisco and London

No.	Author	Title
13	Lange, N.A.	Lange's Handbook of Chemistry, 12th ed. 1979, editor John A. Dean, McGraw-Hill, New York

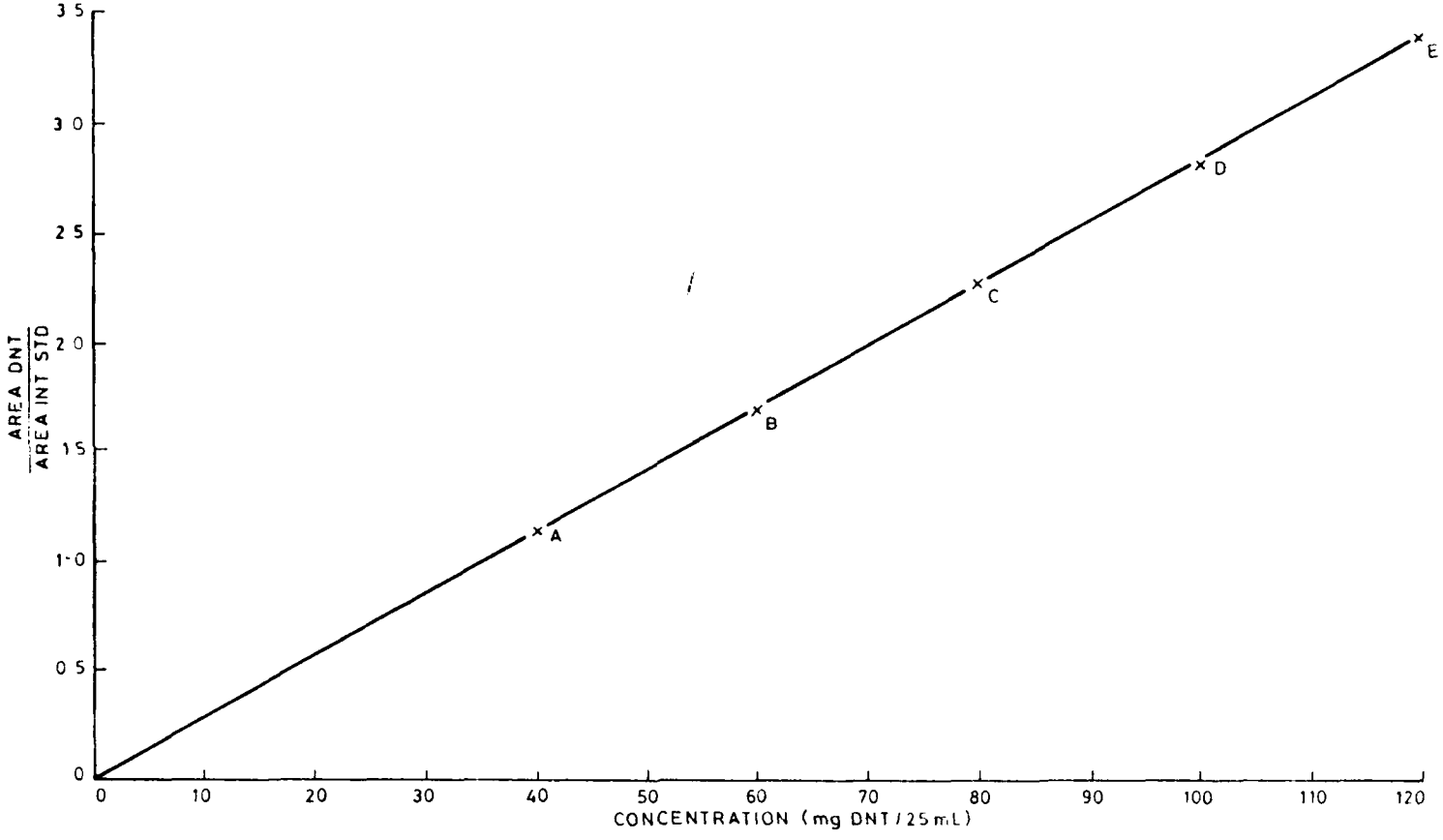


Figure 2. GC - standard calibration graph of area DNT/area int. std. versus concentration of DNT

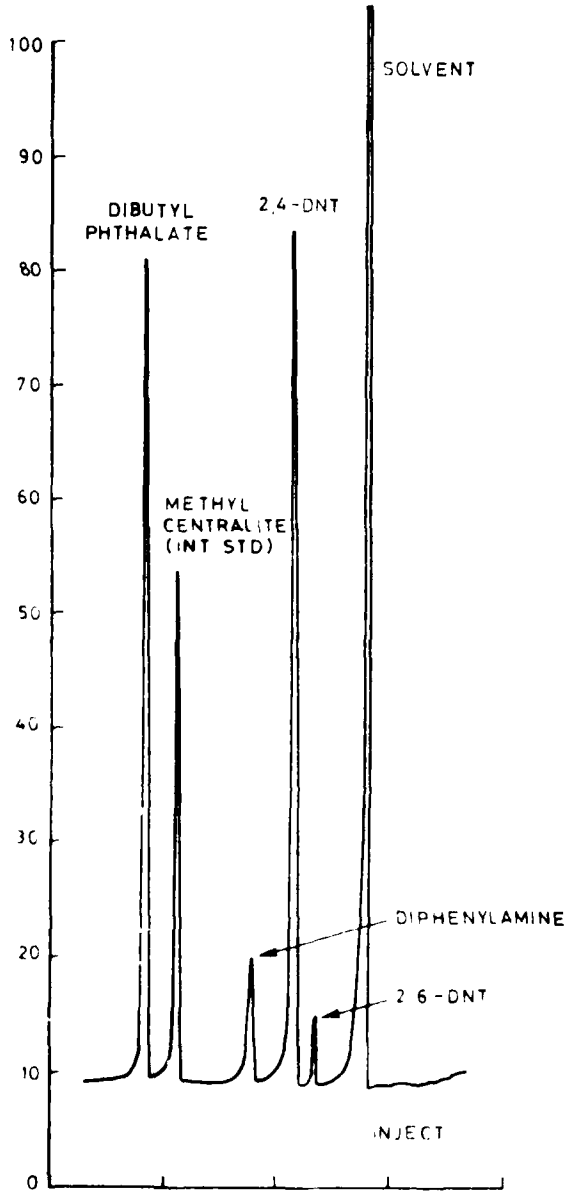


Figure 1. Gas chromatogram of an NH propellant extract

TABLE 2. COMPARISON OF MEAN, STANDARD DEVIATION (SD) AND RELATIVE STANDARD DEVIATION (RSD %) OF % DNT

Sample Number	Propellant Type	Lot No.	Titanous Chloride ($TiCl_3$)	Gas Chromatography	Liquid Chromatography
1	NH033	MEM 1913	Mean 9.77	9.49	9.64
			S.D. 0.063	0.091	0.027
			RSD% 0.64	0.96	0.28
2	NH033	MEM 1948	Mean 10.38	10.06	10.34
			S.D. 0.065	0.084	0.021
			RSD% 0.63	0.83	0.20
3	FNH/PO38	MEM 317	Mean 9.40	8.90	9.49
			S.D. 0.020	0	0.019
			RSD% 0.21	0	0.20
4	FNH023	MEM 1980	Mean 9.72	9.60	9.85
			S.D. 0.101	0.057	0.029
			RSD% 1.04	0.59	0.29
5	AR 2206	MEM 1901	Mean 7.03	7.06	7.09
			S.D. 0.047	0.095	0.015
			RSD% 0.67	1.35	0.21
6	AR 2206	MEM 1965	Mean 6.25	6.19	6.19
			S.D. 0.053	0.082	0.025
			RSD% 0.85	1.32	0.40

TABLE 3. MOBILE PHASE FOR LIQUID CHROMATOGRAPHIC SEPARATION OF DINITROTOLUENE

Time (min)	% dichloromethane	% cyclohexane
0	15.0	85.0
7	15.0	85.0
7.5	90.0	10.0
13.5	90.0	10.0
14.5	15.0	85.0
19.0	15.0	85.0

TABLE 1. DETERMINATION OF % DNT IN SINGLE BASE GUN PROPELLANTS

Sample Number	Propellant Type	Lot No.	Titanous Chloride ($TiCl_3$)	Gas Chromatography	Liquid Chromatography
	C O N T R O L		97.30,99.20,99.50, 100.2 (99.05)	97.80,99.20 (98.5)	98.44,98.73,98.83,98.78,98.42 (98.64)
1	NH033	MEM 1913	9.79,9.83,9.68,9.77	9.41,9.59,9.48	9.59,9.60,9.63,9.64,9.65,9.65,9.66, 9.66
2	NH033	MEM 1948	10.35,10.42,10.25,10.34, 10.40,10.39,10.46,10.42	10.19,10.12,9.99,9.99, 10.12,9.94,10.09,10.05	10.30,10.33,10.32,10.34,10.35,10.36, 10.36,10.33
3	FNH/P038	MEM 317	9.41,9.41,9.41,9.37	8.90,8.90	9.50,9.45,9.47,9.48,9.49,9.50,9.50, 9.50
4	FNH023	MEM 1980	9.77,9.83,9.63,9.63	9.56,9.64	9.82,9.81,9.82,9.83,9.86,9.87,9.88, 9.88
5	AR2206	MEM 1901	7.06,7.06,6.96,7.03	7.13,6.95,7.09	7.06,7.07,7.08,7.08,7.09,7.10,7.10, 7.10
6	AR2206	MEM 1965	6.25,6.25,6.16,6.21	6.19,6.09,6.27,6.13	6.14,6.15,6.17,6.18,6.20,6.20,6.20, 6.20

Note 1. Each value listed represents a single determination. For each propellant type at least two determinations (duplicates) were carried out as a minimum, up to a maximum of eight.

2. The figures in parenthesis ie 99.05,98.5,98.64 are average values for the controls by the three methods, respectively.

APPENDIX V

STATISTICAL TREATMENT (ANALYSIS OF VARIANCE) OF RESULTS - TEST OF SIGNIFICANT DIFFERENCE

Sample Number	$\bar{X}_1$	$\bar{X}_2$	$\bar{X}_3$	S_1	S_2	S_3	S_w	S_b	F	υ_1	υ_2	$F_{0.05}$	$F_{0.01}$	Sig 0.05	Sig 0.01		$\bar{X}_i - \bar{X}_j$	LSD 0.05	LSD 0.01	Sig 0.05	Sig 0.01
1	9.768	9.493	9.635	0.063	0.091	0.027	0.053	0.255	23.2	2	12	3.89	6.93	S	S	$\bar{X}_1 - \bar{X}_2$	0.275	0.088	0.124	S	S
																$\bar{X}_1 - \bar{X}_3$	0.132	0.070	0.099	S	S
																$\bar{X}_2 - \bar{X}_3$	0.142	0.078	0.110	S	S
2	10.379	10.061	10.336	0.065	0.084	0.021	0.062	0.047	61.0	2	21	3.47	5.78	S	S		0.318	0.065	0.089	S	S
																	0.043	0.065	0.089	NS	NS
																	0.275	0.065	0.089	S	S
3	9.400	8.900	9.486	0.020	0	0.018	0.018	0.576	847	2	11	3.98	7.21	S	S		0.500	0.034	0.049	S	S
																	0.086	0.024	0.034	S	S
																	0.486	0.031	0.044	S	S
4	9.715	9.600	9.846	0.101	0.056	0.029	0.060	0.241	16.0	2	11	3.98	7.21	S	S		0.115	0.115	0.162	-	NS
																	0.131	0.081	0.115	S	S
																	0.246	0.105	0.148	S	S
5	7.028	7.057	7.085	0.047	0.095	0.015	0.047	0.067	2.1	2	12	3.89	6.93	NS	NS		0.029	0.078	0.109	NS	NS
																	0.057	0.062	0.087	NS	NS
																	0.028	0.069	0.097	NS	NS
6	6.250	6.186	6.180	0.053	0.082	0.024	0.058	0.110	3.5	2	21	3.47	5.78	S	NS		0.064	0.061	0.082	S	S
																	0.070	0.061	0.082	S	NS
																	0.006	0.061	0.082	NS	NS

both 5% and 1% levels of significance.

Consider, sample 2; the difference between means 1 and 2 is significant at both 5% and 1% levels of significance (ie 0.318 > 0.065, 0.089) whereas the difference between means 1 and 3 is not significant (ie 0.043 < 0.065, 0.089).

Considering the six separate sample types of 3 means each, in 5 cases the F test indicates that the 3 means as a group differ significantly at one or more of the two levels of significance. The standard deviation of such differences is best indicated by the appropriate values of S_b.

In practical terms however, there is no significant difference between any of the three methods because the propellant specification limits are quite wide ie for NH, FNH propellants the specification for DNT contents is 10 ± 1%, and for AR 2206 4-8% DNT. All three methods give results well within these specification limits, and both HPLC and GLC methods are considered as suitable replacements for the $TiCl_3$ method.

APPENDIX IV

STATISTICAL TREATMENT OF RESULTS

In this work, the means obtained for each propellant type by the three methods are compared by an analysis of variance treatment. The results are summarised in Appendix V. Looking at Appendix V, $\bar{X}_1$, $\bar{X}_2$ and $\bar{X}_3$ refer to the means obtained by the $TiCl_3$, GC and HPLC methods, respectively. S_1, S_2 and S_3 refer to the respective standard deviations.

S_w is the within samples standard deviation, and S_b is the between samples means standard deviation. F is the variance ratio, ie

$$F = \frac{S^2_b}{S^2_w}$$

ν_1 and ν_2 are the degrees of freedom where

$\nu_1 = k - 1$ (where k is the number of methods compared (3))

and $\nu_2 = N - k$ (where N is the total number of individual measurements being considered)

$F_{0.05}$ and $F_{0.01}$ (with the appropriate degrees of freedom) are obtained from tables of the F-distribution(ref.12,13) at the 5% and 1% level of significance, respectively.

Thus, in cases where the calculated F exceeds the $F_{0.05}$ or $F_{0.01}$ found in tables, a significant difference exists between some of the means at the 5% or 1% or both levels of significance.

From Appendix V, for samples 1, 2, 3 and 4 the F ratio exceeds the $F_{0.05}$ and $F_{0.01}$; for sample 5, $F < F_{0.05}$, $F_{0.01}$ and for sample 6 the result is marginal. This means that only the sample 5, the three means do not differ significantly at either the 5 or 1% level of significance. In the case of sample 6, a significant difference between the three means exists at the 5% level but not at the 1% level of significance.

In order to find out which pair of means ($\bar{X}_1\bar{X}_2$, $\bar{X}_1\bar{X}_3$ or $\bar{X}_2\bar{X}_3$) is signficantly different, the least significant difference (LSD) is calculated and compared with the difference between the means.

$$LSD = \sqrt{\frac{n_1 + n_2}{n_1 n_2} S^2_w \quad F\nu_1=1, \quad \nu_2=N-k}$$

Thus for sample 1, the difference between means 1 and 2 is

$$|\bar{X}_1 - \bar{X}_2| = 0.275$$

which is greater than the LSD at 0.05 (0.088) and LSD at 0.01 (0.124). Therefore a significant difference exists between means 1 and 2 (sample 1) at

p-nitrotoluene	200 s
2,6-dinitrotoluene	320 s
2,4-dinitrotoluene	393 s
diphenylamine	713 s
dibutyl phthalate	777 s

A typical chromatogram is shown in figure 3. In most cases the printer was stopped just after elution of the 2,4-DNT - consequently, no diphenylamine or dibutyl phthalate peaks are seen in figure 3 - the mobile phase, however, was continued for sufficient time to ensure that these components were eluted from the column.

III.4.7 Prepare a series of calibration standards from a stock solution of 2,4-dinitrotoluene (2 g) in dichloromethane (100 mL). Transfer by pipette 2, 3, 4 and 5 mL of this solution to 25 mL volumetric flasks, add 5 mL of p-nitrotoluene internal standard solution (solution 2.4 above) and make up to volume with dichloromethane. Check that a linear response is obtained over the range of standards. If excessive non-linearity (>5%) is observed, further dilution of the solutions is required.

III.4.8 Prepare a control from the above stock (solution 4.7 above) by pipetting 5 mL into a 25 mL volumetric flask, add internal standard and make up to volume.

III.4.9 Prepare two solutions, containing equal amounts of 2,6-dinitrotoluene and 2,4-dinitrotoluene in dichloromethane. Inject, and measure the detector response. In this case the response is not equal - the response of 2,6-dinitrotoluene is only approximately 38% that of 2,4-dinitrotoluene.

III.4.10 Prepare a calibration standard by weighing out 100 mg of 2,6-dinitrotoluene and 1.9 g of 2,4-dinitrotoluene - make up to 100 mL with dichloromethane. Transfer by pipette 5 mL of this solution to a 25 mL volumetric flask, add 5 mL of internal standard solution and make up to volume.

III.5 Expresssion of results

III.5.1 Calculate the percentage of dinitrotoluene in the propellant by utilising the microprocessor controlled software "Method 3, SP8000 Data System". Correct for added matter, by multiplying by $\frac{100}{100 - \%\ \text{added matter}}$. The percent added matter is obtained from the referencing specification.

APPENDIX III

DETERMINATION OF DINITROTOLUENE BY HIGH PERFORMANCE LIQUID CHROMATOGRAHPY

III.1 Principle

III.1.1 The propellant is extracted with dichloromthane. An internal standard is added and the mixture is separated by high performance liquid chromatography.

III.2 Reagents

III.2.1 Solvents - Ajax "Unichrom - specially purified for HPLC", dichloromethane, cyclohexane.

III.2.2 2,6-dinitrotoluene - AR grade.

III.2.3 2,4-dinitrotoluene - AR grade.

III.2.4 p-nitrotoluene AR grade. (For use as internal standard, 0.5 g in 100 mL dichloromethane.)

III.3 Apparatus

III.3.1 See Appendix I for a description of the extraction apparatus.

III.3.2 Liquid chromatograph - Spectra-Physics SP8000A.

III.3.3 Column - Hibar, Lichrosorb (Merck) Si 100 (10 µm), column length 250 mm, internal diameter 4 mm.

III.3.4 Detector SP8400 UV/vis operating at 254 nm.

III.4 Procedure

III.4.1 Prepare and extract about 5 g of propellant as described in Appendix I (4.2.1 and 4.2.2).

III.4.2 Concentrate the dichloromethane extract, transfer to a 25 mL volumetric flask and dilute to volume.

III.4.3 Transfer 5 mL to a 25 mL volumetric flask and add 5 mL of internal standard solution (0.5 g p-nitrotoluene in 100 mL dichloromethane). Dilute to volume.

III.4.4 Filter a small portion of the mixture through a membrane filter (0.45 micron) and inject on to the column (using 10 µL loop injector).

III.4.5 Liquid chromatography conditions:

Column temperature 50°C. Binary mobile phase as in Table 3. The solvents were degassed with helium. A constant flow mode of 2 mL/min was used.

III.4.6 With the above conditions, the following representative retention times were obtained :

2,6-dinitrotoluene	172 s
2,4-dinitrotoluene	234 s
diphenylamine	355 s
methyl centralite	532 s
dibutyl phthalate	628 s

II.4.7 Prepare a series of calibration standards from a stock solution of 2 g of 2,4-dinitrotoluene in dichloromethane (100 mL). Transfer by pipette 2, 3, 4, 5 and 6 mL of this solution to 25 mL volumetric flasks, add 5 mL of internal standard solution (solution 2.5 above), and make up to volume with dichloromethane. Check that a linear response is obtained over the range of standards (figure 2).

II.4.8 Prepare a control by dissolving 1 g 2,4-dinitrotoluene in 100 mL dichloromethane. Transfer 10 mL to a 25 mL volumetric flask, add 5 mL internal standard and make up to volume.

II.4.9 Prepare two solutions, containing equal amounts of 2,6-dinitrotoluene and 2,4-dinitrotoluene in dichloromethane. Inject, and measure the detector response - in this case the response is equal, ie one can add the areas of 2,6- and 2,4-dinitrotoluene to obtain total dinitrotoluene.

II.5 Expression of results

II.5.1 Calculate the percentage of dinitrotoluene in the propellant as follows :

$$\% \text{ DNT} = \frac{\text{area sample peak}}{\text{area int std peak x slope}} \times \frac{0.5}{\text{wt propellant}} \times \frac{100}{100 - \% \text{ added matter}}$$

where slope = slope of line in figure 2.

APPENDIX II

DETERMINATION OF DINITROTOLUENE BY GAS CHROMATOGRAPHY

II.1 Principle

II.1.1 The propellant is extracted with dichloromethane. An internal standard is added and the mixture is separated by gas chromatography.

II.2 Reagents

II.2.1 All reagents were checked to ensure they were homogeneous by gas chromatography.

II.2.2 Dichloromethane - AR grade.

II.2.3 2,6-dinitrotoluene - AR grade.

II.2.4 2,4-dinitrotoluene - AR grade.

II.2.5 Methyl centralite - mp 121.5 - 122°C recrystallised from boiling ethanol/petroleum spirit (for use as internal standard, 2.5 g in 500 mL dichloromethane).

II.3 Apparatus

II.3.1 See Appendix I for a description of the extraction apparatus.

II.3.2 Gas chromatograph - Perkin Elmer F11 with flame ionisation detector.

II.3.3 Integrator - Hewlett Packard 3307A (electronic).

II.3.4 Column - stainless steel column 2 m x 3 mm OD packed with 3% OV-101 on Chromosorb W HP 100-120 mesh.

II.4 Procedure

II.4.1 Prepare and extract about 5 g of propellant as described in Appendix I (4.2.1 and 4.2.2).

II.4.2 Concentrate the dichloromethane extract, transfer to a 25 mL volumetric flask and dilute to volume.

II.4.3 Transfer 5 mL to a 25 mL volumetric flask and add 5 mL of internal standard solution (2.5 g methyl centralite in 500 mL dichloromethane). Dilute to volume.

II.4.4 Inject 1µL of solution onto the column and measure the area of the dinitrotoluene peaks and internal standard using the electronic integrator.

II.4.5 Gas chromatography conditions

Column temperature 150°C initial, hold 5 min, program to 200°C at 15°/min. Injector, detector at 200°C. Nitrogen carrier gas at 30 mL/min.

II.4.6 With the above conditions, the following representative retention times were obtained:

m = mass of propellant sample taken (usually 2-4.0 g, or 0.2 g for control)

The percent added matter is obtained from the referencing specification.

NOTES: 1. Because of the high coefficient of expansion of ethanol it is necessary to take particular care to avoid errors due to volume changes arising from minor variations in temperature.

2. Preparation of 0.2 N Titanous chloride

2.1 Mix 200 mL of commercial titanous chloride solution (approximately 15%) with 80 mL of concentrated hydrochloric acid. Filter if necessary quickly through No.1 paper, and make up to 800 mL with water. Pass a slow stream of nitrogen through the solution whilst boiling on a hot plate for 10 min until the issuing vapours no longer colour moist lead acetate paper. Cool and store under nitrogen in a dark, well-stoppered bottle.

3. Standardisation of 0.15 M Ferric Ammonium Sulphate

3.1 Dissolve approximately 72.3 g of ferric ammonium sulphate in 1 L of water containing 26.6 mL of concentrated sulphuric acid (ie dilute sulphuric acide solution 1 N). The ferric ammonium sulphate dissolves with difficulty and is best carried out by heating and stirring the solution for approximately 3 hours.

3.2 Standardise the ferric ammonium sulphate solution by reduction with zinc amalgam followed by titration of the resulting ferrous salt with standard 0.1 N potassium dichromate.

3.3 Prepare zinc amalgam by warming 4 g of zinc turnings, 100 g of mercury and 200 mL of 20% sulphuric acid on a water bath until all the zinc has dissolved (approximately 1 hour). Pour off the acid, wash the amalgam with water and transfer it to a 100 mL glass stoppered bottle.

Rinse out the bottle containing the amalgam with small quantities of the solution of ferric ammonium sulphate (green colour) to be standardised and then half fill the bottle with fresh solution. Replace the stopper and shake vigorously (5 min) until complete reduction to the ferrous condition (blue colour) has been achieved.

Withdraw 20 mL of the reduced solution by means of a pipette and transfer to the titration flask connected to a slow flow of nitrogen. Add 10 mL of concentrated sulphuric acid, cool the mixture and titrate with 0.1 N potassium dichromate (4.904 g in 1 L water) using 2 drops of o-phenanthroline ferrous sulphate ("ferroin" 0.025 M) as indicator. The colour change at the end is from pink to green.

I.4.2 Propellant

I.4.2.1 If necessary, (for NH, FNH propellants), grind the propellant (in a cordite mill) and sieve using the 2 mm sieve and receiving pan. (The AR 2206 propellants, being small grained, were not ground or sieved.)

I.4.2.2 Weigh out an appropriate amount of propellant (usually 2-4.0 g) to contain approximately 0.2 g of dinitrotoluene into a tared alundum thimble. (This is an amount which gives convenient titration volumes.) Record the mass to the nearest 0.1 mg.

Place the thimble in a cold Soxhlet extraction apparatus and extract with 150 mL of dichloromethane for 70 hours on a water bath.

I.4.2.3 Gently boil off the dichloromethane solvent to dryness, dissolve the residue in ethanol and transfer quantitatively to a 100 mL volumetric flask. Make up to volume with ethanol (Note 1). (Use 20 mL of this solution in the subsequent reduction procedure.)

I.4.2.4 Transfer by pipette 20 mL of the control solution or propellant extract to the titration flask connected to a flow of nitrogen. Continue a slow flow of nitrogen until the determination is complete.

I.4.2.5 Add 25 mL of titanous chloride solution (Note 2) followed by 25 mL of hydrochloric acid.

I.4.2.6 Connect the flask to the reflux condenser and boil gently (15 min) on a heating mantle.

I.4.2.7 Without disconnecting the flask from the condenser remove the flask from the mantle and cool to room temperature.

I.4.2.8 Wash the condenser with 30 mL of ethanol and then remove the flask from the condenser.

I.4.2.9 Add 5 mL of ammonium thiocyanate. Titrate with ferric ammonium sulphate solution (Note 3) to the end-point as indicated by the permanent red colour.

I.4.2.10 Carry out a blank determination omitting the propellant extract.

I.5 Expression of results

I.5.1 Calculate the percentage of dinitroluene in the propellant as follows :

$$\% \text{ DNT} = \frac{7.59 \times M \times (B-T) \times 100}{m \times (100 - \% \text{ added matter})}$$

where B = volume of ferric ammonium sulphate solution used for blank, mL

T = volume of ferric ammonium sulphate solution used for sample aliquot, mL

M = molarity of ferric ammonium sulphate solution

APPENDIX I

DETERMINATION OF DINITROTOLUENE BY TITANOUS CHLORIDE REDUCTION

I.1 Principle

I.1.1 The propellant is extracted with dichloromethane. The solvent is evaporated and the residue is made up to volume with ethanol. An aliquot of this ethanol solution is then reduced by boiling with an excess of titanous chloride. The amount of titanous chloride used for reduction is determined by back titration with ferric ammonium sulphate solution and is used to calculate the amount of dinitrotoluene present.

I.2 Reagents

I.2.1 Dichloromethane - AR grade.

I.2.2 Ethanol - 95% v/v at 15.5°C to BS507.

I.2.3 Inert gas - nitrogen (oxygen free).

I.2.4 Titanous chloride - approximately 0.2 M, in 4% m/V hydrochloric acid solution.

I.2.5 Ammonium thiocyanate solution - (20% m/V, aqueous).

I.2.6 Ferric ammonium sulphate - 0.15 M, standard solution in 0.5 M sulphuric acid solution.

I.2.7 Potassium dichromate - 0.1 N.

I.2.8 2,4-Dinitrotoluene - m.p. 70-70.5°C (Fluka, puriss or equivalent).

I.2.9 Zinc amalgam.

I.2.10 o-phenanthroline ferrous sulphate ("ferroin" 0.025 M).

I.3 Apparatus

I.3.1 Titration flask (250 mL) - 3-necked - containing inlet for nitrogen, condenser, stopper and magnetic stirrer bar.

I.3.2 Heating mantle.

I.3.3 Magnetic stirrer.

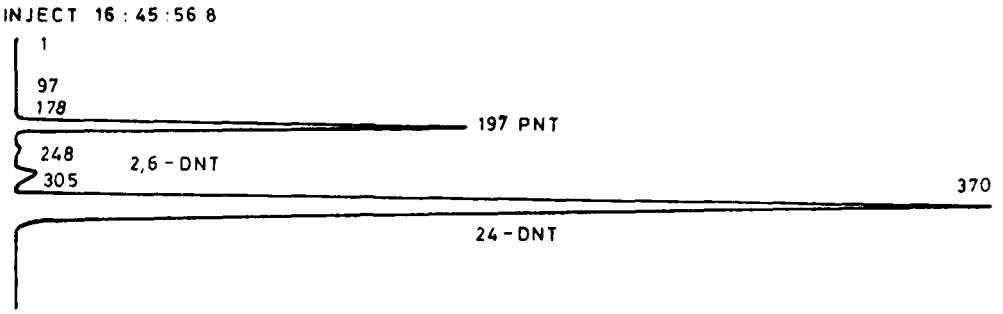
I.3.4 Soxhlet extraction apparatus - alundum thimble, round bottom flask (250 mL, 1 neck) condenser.

I.3.5 Water bath.

I.4 Procedure

I.4.1 Control

I.4.1.1 Weigh out 0.2 g of 2.4-dinitrotoluene, transfer to a 100 mL volumetric flask and make up to volume with ethanol. (Use 20 mL of this solution in the subsequent reduction procedure.)



NITROTOLUENES AUG-07-81 16:45

CHANNEL 1 RUN 9 FILE 2 METHOD 3

INDEX B SAMPLE FNH023 MEM1980

S,AMT= 1

NAME	CONC	RT	AREA		KF	RRT
1		97	492			0.492
2		178	611	1		0.903
INTERNAL		197	902564	IS		1
4		248	11521			1.259
2,6DNT	4.387	305	90512	1	43.75	1.548
2,4DNT	94.2	370	4520207	L	18.81	1.878
TOTALS	98.59		5525907			

NITROTOLUENES AUG-07-81 16:45

CHANNEL 1 RUN 9 FILE 2 METHOD 3

INDEX B SAMPLE FNH023 MEM1980

NAME	AVERAGE	REL SD %	STD DEV	VARIANCE
INTERNAL				
2,6DNT	4.385	0.451	0.02	< 0.001
2,4DNT	93.69	0.594	0.557	0.309

Figure 3. HPLC Chromatogram (top) and data printout (below) of an FNH propellant extract

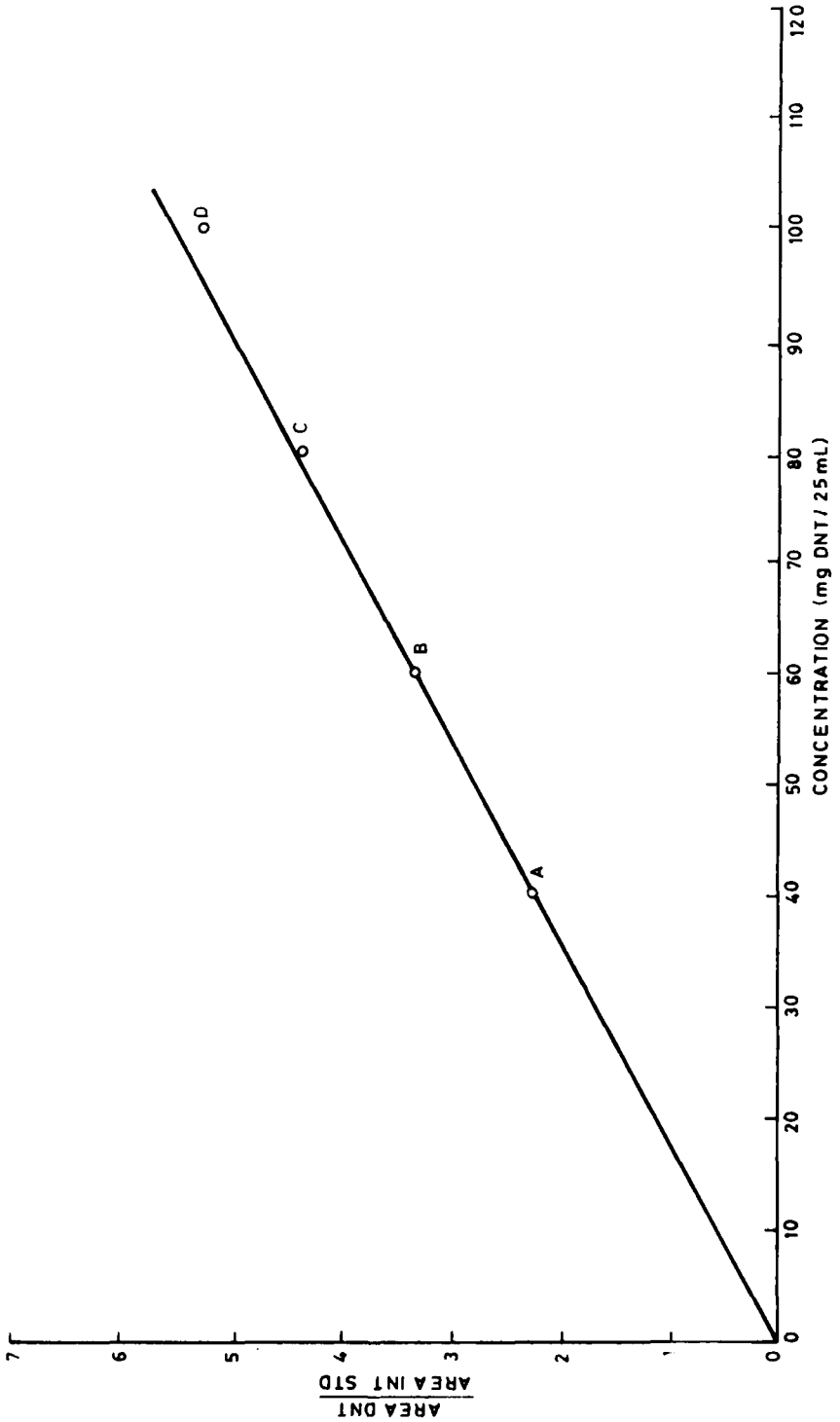


Figure 4. HPLC - standard calibration graph of area DNT/area int. std. versus concentration of DNT

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Security classification of this page: UNCLASSIFIED

1 DOCUMENT NUMBERS	2 SECURITY CLASSIFICATION
AR Number: AR-004-086	a. Complete Document: Unclassified
Series Number: WSRL-0368-TM	b. Title in Isolation: Unclassified
Other Numbers:	c. Summary in Isolation: Unclassified

3 TITLE

THE DETERMINATION OF DINITROTOLUENE IN SINGLE BASE PROPELLANTS

4 PERSONAL AUTHOR(S):

M. Mular

5 DOCUMENT DATE:

June 1984

6 6.1 TOTAL NUMBER OF PAGES: 23

6.2 NUMBER OF REFERENCES: 13

7 7.1 CORPORATE AUTHOR(S):

Weapons Systems Research Laboratory

7.2 DOCUMENT SERIES AND NUMBER

Weapons Systems Research Laboratory 0368-TM

8 REFERENCE NUMBERS

a. Task: DEF 80/124

b. Sponsoring Agency: DEF

9 COST CODE:

10 IMPRINT (Publishing organisation)

Defence Research Centre Salisbury

11 COMPUTER PROGRAM(S) (Title(s) and language(s))

12 RELEASE LIMITATIONS (of the document):

Approved for Public Release

Security classification of this page: UNCLASSIFIED

Security classification of this page: UNCLASSIFIED

13 ANNOUNCEMENT LIMITATIONS (of the information on these pages):

No limitation

14 DESCRIPTORS:

a. EJC Thesaurus Terms

Propellants
Dinitrotoluene
chemical analysis
Gas chromatography
Liquid chromatography

b. Non-Thesaurus Terms

Single base propellants
Titanous chloride reduction

15 COSATI CODES:

19010

16 SUMMARY OR ABSTRACT:
(if this is security classified, the announcement of this report will be similarly classified)

Six single base gun propellants of three different types (AR 2206, NH and FNH) were analysed for dinitrotoluene by three different methods, viz titanous chloride reduction, gas chromatography and high performance liquid chromatography (HPLC). In general, similar results were obtained by all three methods.

Although any of the three methods can be used for the determination of dinitrotoluene, the HPLC method is recommended - the equipment is automated and microprocessor controlled, and analyses can be performed relatively quickly, with good precision and with the lowest relative standard deviation of the order of 0.3%. It is recommended that the HPLC method be adopted as a standard test method.

Security classification of this page: UNCLASSIFIED

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