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MINISTRY OF DEFENCE

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

TECHNICAL REPORT No 122

The Identification of Traces of Explosives by Field Spot Tests

J L McDougall
R J J Simkins

Dr Anthony J. Finnerty
3 DL
BRL

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MINISTRY OF DEFENCE

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

Technical Report No 122

March 1973

The Identification of Traces of Explosives by Field Spot Tests

by

J L McDougall
R J J Simkins

SUMMARY

The detection and identification of traces of explosives by means of colorimetric spot tests performed upon an adhesive tape substrate have been examined. The adhesive tape serves as a very effective means of collecting a sample, either from suspect material, a working surface, or from the skin of a suspect. Nineteen explosives were examined, these being chosen as representative of military, commercial and amateur explosives. Nineteen different tests were examined, and with the exception of ammonium perchlorate all the explosives considered were found to give a positive response to some, but not all tests. A scheme of analysis was devised that would separate all the candidate explosives. While the investigation has greatly increased the number of spot tests known to be suitable for colorimetric reactions on an adhesive tape substrate, consideration has shown that a multiplicity of tests is not necessarily suitable for use by non-scientists for field testing. Limited, but adequate identification of most explosives may be obtained using only two of the tests. In the course of the investigation a new colorimetric test for RDX and HMX was discovered, and one for perchlorates; in addition, the suitability of an existing test for cyanides for the detection of nitroaromatics was exploited.

Further copies of this technical report can be obtained from Defence Research Information Centre, Station Square House, St Mary Cray, Orpington, Kent. BR5 3RE

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1 INTRODUCTION

We have described elsewhere[1,2] some simple colorimetric tests that may be used for the identification in the field of explosive substances. The amounts of sample required are not large (5 to 100 mg), but they do necessitate a discrete amount of sample. Information has been received from the United States Embassy about a detection technique in which the suspect sample is picked up by application of white plastic adhesive tape, and spot tests then conducted directly on the tape surface. The technique is very sensitive, and traces of TNT have been detected, even after several hand washings, on the skin of a subject who had handled it.

As described to us the technique was very good for TNT (the test being the blood red colour produced by application of alcoholic potassium hydroxide) and moderately successful for RDX (a straw colour being produced by the action of a solution of J-acid in concentrated sulphuric acid). Interference from other contaminents was minimal, but the test was regarded as being limited to explosives of the TNT or RDX type.

The advantages of the tape technique for providing a suitable sample substrate for colorimetric tests were immediately obvious, and it seemed worthwhile investigating whether other types of explosives could be detected in this way.

2 METHODS

Compounds selected for testing were chosen on the basis that they might be procured from military stores, from civil engineering stores, or from amateur sources. The compounds so chosen are listed below; the materials were chosen as being representative, and the list is not totally comprehensive.

Military Stores: Ammonium Picrate
Ammonium Perchlorate
1,3-Dinitrobenzene
2,4-Dinitrophenol
2,4-Dinitrotoluene
Dipicrylamine
Ethylenediamine dinitrate
Ethylenedinitramine
2,4,6-Trinitrotoluene
Tetryl
RDX
HMX

Commercial Explosives:	Black Powder Submarine Blasting Dynamite Polar Ammon Gelatine Dynamite PETN
Amateur Sources:	Ammonium Nitrate Picric Acid Sodium Chlorate

A roll of 2 in white plastic adhesive tape (3 M's 850, as supplied by the US Embassy) was used for sampling the test material. Three modes of sampling were used: the addition of a few microcrystals directly to the sticky surface, pressing the sticky surface of the tape onto a bare wooden surface onto which a few crystals of the material had been crushed and then wiped off, and pressing the sticky surface of the tape onto the skin of the hands of an operator who had been handling the material. For testing three or four separate drops of the reagent were added to the tape at those places where discoloration suggested that there might be a sample, while simultaneously a drop was placed on a known clean area to serve as a reference blank. Apart from the obvious difference in intensity all three sampling methods seemed effective.

Nineteen different colorimetric tests were investigated, and in some cases the effect of the prior addition of a solvent was also tried, so that in total about two thousand experiments were performed. The criterion for a successful test was taken as being a colour change sufficiently distinct from the blank that an unexperienced operator could unequivocally detect it.

3 EXPERIMENTAL

All reagents are Analytical Grade unless otherwise stated.

3 1 Alcoholic KOH Test

Reagent. Dissolve 10 g of potassium hydroxide in 100 cm^3 absolute alcohol; the resultant solution should be colourless.

Add one drop of reagent to tape and observe any colour formation; perform a parallel blank test. The appearance of a dark red colour is regarded as a positive test, but violet and transient blue shades also occur as positive reactions. Dinitrophenol and picric acid give only a deep yellow colour, but this is distinct from any original yellow. For detailed results cf Table 1.

3 2 Azulene Test

Reagents. Dissolve 0.4 g of 4-nitroaniline in 100 cm^3 of glacial acetic acid. Dissolve 0.08 g of azulene in 100 cm^3 of acetic acid (shelf life ca 1 week). Alcoholic KOH as above (3 1). Dilute hydrochloric acid.

Add one drop of alcoholic KOH to the tape, wait for 1 minute and add one drop of dilute hydrochloric acid to the same place, followed immediately by one drop of p-nitroaniline solution. Add one drop of azulene solution and observe any colour change over 1 minute. Change of the original blue to red, green or yellow is regarded as positive. For detailed results cf Table 2.

3 3 Diphenylbenzidine Test

Reagents. A saturated solution of diphenylbenzidine in glacial acetic acid. Concentrated sulphuric acid.

Add one drop of diphenylbenzidine to the tape, wait for 1 minute, and add 1 drop of sulphuric acid to the same place; observe any colour formation. The appearance of a blue or violet colour is regarded as positive. For detailed results cf Table 3.

3 4 Vanadous Sulphate Test

Reagents. Zinc amalgam - mix together 150 g mercury, 10 g zinc and 10 cm^3 of 25% sulphuric acid. Heat on a boiling water bath until the amalgamation is complete, and then store under dilute sulphuric acid. Vanadous sulphate - dissolve 1 g vanadium pentoxide in 50 cm^3 of dilute sulphuric acid by heating on a hotplate. Diphenylamine-I solution as below (3 9).

Prepare a fresh solution of hypovanadous sulphate by adding the vanadous sulphate solution to zinc amalgam in a stout glass bottle and shaking the stoppered bottle for a few minutes. On reduction the vanadous sulphate solution becomes greenish-blue in colour. Add one drop of the hypovanadous solution to the tape and then immediately add one drop of diphenylamine solution to the same place. The appearance of flecks of blue colour which fade after about 1 minute is a positive reaction; if the colour is permanent the test should be regarded as negative as regards the presence of perchlorate ion. For detailed results cf Table 4.

3 5 Thymol Test

Reagents. Dissolve 10 g thymol in 100 cm^3 of acetone. Nitrogen free concentrated sulphuric acid.

Add one drop of thymol solution to the tape, leave for 1 minute, then add one drop of sulphuric acid and observe any colour formation. The appearance of a green or violet colour is regarded as positive; the blank gives a brick-red colour and some care is necessary to distinguish the violet. For detailed results cf Table 5.

3 6 Janovsky Test

Reagents. Alcoholic KOH as above (3 1). Acetone.

Add one drop of acetone to the tape and to this add one drop of alcoholic KOH, observe any colour formation. The appearance of a deep maroon colour is regarded as positive, violet and blue tints do occur as positive reactions. Picric acid gives a maroon colour, and dinitrophenol an intense yellow. For detailed results cf Table 6.

3 7 J-acid Test

Reagent. Dissolve 0.1 g of J-acid (6-amino-1-naphthol-3-sulphonic acid) in 100 cm^3 concentrated sulphuric acid.

Deionized water. Add one drop of reagent to tape, and observe any colour formation over 1 minute. Add one drop of water to the edge of the J-acid drop and observe any change in colour over 1 minute. Perform a parallel blank test. The appearance of a yellow to brown colour is regarded as a positive test. For detailed results cf Table 7.

3 8 Nessler's Test

Reagents. To a thin paste of 10 g of mercuric iodide in a little water add 5 g potassium iodide. To the resultant solution add a solution of 20 g sodium hydroxide in 80 cm^3 of water, and make up to 100 cm^3. Store the turbid solution for a few days, then decant and keep in a dark bottle. Sodium hydroxide - 30% aqueous solution.

Add one drop of sodium hydroxide to the tape and then one drop of Nessler's reagent. A yellow or orange colour is regarded as positive. Nitroaromatics give similar colours to the ammonium salts. For detailed results cf Table 8.

3 9 Diphenylamine-I Test

Reagent. Dissolve 1 g diphenylamine in 100 cm^3 of concentrated sulphuric acid.

Add one drop of diphenylamine-I solution to tape and observe any colour formation. The appearance of a blue or violet colour is regarded as positive. For detailed results cf Table 9.

3 10 Diphenylamine-II Test

Reagent. Dissolve 0.2 g diphenylamine in 100 cm^3 of 85% phosphoric acid.

Add one drop of diphenylamine-II solution to the tape and observe any colour formation. The appearance of a blue or violet colour is regarded as positive. For detailed results cf Table 10.

3 11 Griess Test

Reagents. Dissolve 1 g sulphanilic acid in 100 cm^3 of warm 30% acetic acid. Dissolve 0.03 g 1-naphthylamine by boiling with 70 cm^3 water, decant the colourless solution from the blue-violet residue and dilute with an equal volume of 30% acetic acid. Devarda's alloy.

Add one drop of each solution together on the tape, and then place a speck of Devarda's alloy in the middle of the combined drops; observe any colour formation after a few minutes. The appearance of a red colour is regarded as positive. For detailed results cf Table 11.

3 12 Franchimont Test

Reagents. Dissolve 1 g N,N-diethylaniline in 100 cm^3 glacial acetic acid. Devarda's alloy.

Add one drop of solution to tape and place a speck of Devarda's alloy in the centre of the drop, observe any colour formation. The appearance of red or green colour is regarded as positive. For detailed results cf Table 12.

3 13 Azide/iodine Test

Reagent. Dissolve 3 g sodium azide in 100 cm^3 of 0.1 N iodine solution.

Add one drop to the tape and observe closely whether it becomes cloudy; the use of a hand lens is advisable. The evolution of gas, as evidenced by cloudiness or the appearance of distinct bubbles, is regarded as a positive test. For detailed results cf Table 13.

3 14 Manganous Sulphate Test

Reagents. Saturated solution of manganous sulphate in water. Syrupy phosphoric acid. Dissolve 1 g diphenylcarbazide in 100 cm^3 of ethanol.

Add one drop of manganous sulphate solution to the tape, and to this add one drop of phosphoric acid; leave for 1 minute, observe the colour and add 1 drop of diphenylcarbazide solution and note any colour change. The appearance of a red colour is regarded as positive. For detailed results cf Table 14.

3 15 SPAF Test

Reagent. Prepare a fresh solution of 1 g sodium pentacyanoammineferroate (SPAF) in water. Acetone.

Add one drop of acetone to tape and then one drop of SPAF solution and observe any colour formation. The appearance of a yellow to brown colour is regarded as positive. For detailed results cf Table 15.

3 16 Diphenylamine-III Test

Reagent. Dissolve 0.2 g of diphenylamine in 100 cm^3 of 70% sulphuric acid.

Add one drop of reagent to tape, and observe any colour formation. The appearance of a blue colour is regarded as positive. For detailed results cf Table 16.

3 17 Cyanide Test

Reagents. Dissolve 1 g of sodium cyanide and 2 g of sodium carbonate in 100 cm^3 of water. Ethanol.

Add one drop of cyanide solution to the tape and observe any colour formation. Repeat adding one drop of ethanol first. The appearance of a reddish brown colour is regarded as positive. For detailed results cf Table 17.

3 18 ABPHSA Test

Reagents. Dissolve 0.18 g of azobenzenephenylhydrazine sulphonic acid in 100 cm^3 of water. Concentrated sulphuric acid.

Add one drop of sulphuric acid to the tape, wait for one minute, and add one drop of the ABPHSA and observe any colour formation. The appearance of a red or blue colour would be regarded as positive. For results cf Table 18.

3 19 Riegler's Test

Reagents. Dissolve 1 g of p-nitroaniline and 2 cm^3 of dilute hydrochloric acid in 20 cm^3 of warm water, using vigorous shaking. After cooling mix with an equal volume of 3% aqueous sodium nitrite solution, and shake to dissolve the products; filter before use. Calcium oxide.

Place one drop of reagent on tape and to its centre add a speck of calcium oxide. The formation of a red ring around the calcium oxide particle would be regarded as positive. For results cf Table 18.

3 20 Testing for Post-explosion Residues

When the azide-iodine test (3 13) was used for testing the residue from burnt black powder, a more positive test was obtained than with unburnt material.

3 21 Addition of Solvent Prior to Tests

The addition of one drop of solvent to the tape before performing the tests was examined. The solvents tried were acetone, cyclohexanone and dimethylformamide; the tests to which this variation was applied were the alcoholic KOH (3 1), the azulene (3 2), J-acid (3 7), diphenylamine-I (3 9), diphenylamine-II (3 10), and Griess (3 11). In the case of alcoholic KOH the effect of a prior addition of acetone markedly altered some of the colours produced, and this technique became a separate test - Janovsky (3 6). In nearly all cases the use of cyclohexanone was inadvisable, since it produced brown colouration in the blanks as well as in the tests. In the case of HMX the use of acetone prior to the azulene tests gave rise to a red colour, thus showing that the difference normally observed between RDX and HMX in this test is due to solubility factors. In most other cases the effect of solvent was to concentrate the colour in a ring round the edge of the drop. Prior addition of ethanol speeded the response for reactive compounds in the cyanide test (3 17).

3 22 Use of J-acid Solution in Place of Sulphuric Acid

Since the J-acid solution (3 7) is one of concentrated sulphuric acid, the effect of using this solution in place of pure concentrated sulphuric acid was examined for the diphenylbenzidine (3 3) and thymol (3 5) tests was examined. Slight differences in colour produced were noticeable, the most distinct being a yellow-green obtained with gelatine sub-blasting dynamite in place of a deep green, but in general no marked interference was found.

3 23 Results

Detailed observation on the colours produced in the various tests are given in Tables 1 - 18. The results are summarized in terms of positive or negative response in Table 19. It should be noted that there are often subtle differences in response that are not shown in Table 19.

TABLE 1

COLOUR REACTION OF EXPLOSIVES WITH ALCOHOLIC KOH (3 1)

Explosive	Colour	Remarks
Blank	Nil	
Ammonium nitrate	Nil	
Ammonium perchlorate	Nil	
Ammonium picrate	Yellow	Colour produced by soln rather than reaction
Black powder	Nil	
Dinitrobenzene	Violet	
Dinitrophenol	Yellow	Colour produced by soln
Dinitrotoluene	Dark brown	Transient blue may be observed before brown
Dipicrylamine	Deep reddish/ violet	
Submarine blasting dynamite	Nil	
Polar ammon gelatine dynamite	Nil	
Ethylenediamine dinitrate	Nil	
Ethylenedinitramine	Nil	
HMX	Nil	
Picric acid	Orange-yellow	
PETN	Nil	
RDX	Nil	
Sodium chlorate	Nil	
Tetryl	Bright maroon	
TNT	Dark red	

TABLE 2

COLOUR REACTIONS OF EXPLOSIVES WITH AZULENE (3 2)

Explosive	Colour	Remarks
Blank	Light blue	
Ammonium nitrate	As blank	
Ammonium perchlorate	As blank	
Ammonium picrate	As blank	
Black powder	As blank	
Dinitrobenzene	As blank	
Dinitrophenol	As blank	
Dinitrotoluene	As blank	
Dipicrylamine	As blank	
Submarine blasting dynamite	Reddish-violet	Straight nitroglycerine gives violet-red colour
Polar ammon gelatine dynamite	Reddish-violet	
Ethylenediamine dinitrate	As blank	
Ethylendeinitramine	As blank	
HMX	As blank	Prior addn 1 drop Me_2CO gives yellow-green
Picric acid	As blank	
PETN	As blank	
RDX	Reddish-violet	Prior addn 1 drop Me_2CO gives same colour
Sodium chlorate	Bright green	Colour is transient, turning yellow
Tetryl	As blank	
TNT	As blank	

TABLE 3

COLOUR REACTIONS OF EXPLOSIVES WITH DIPHENYLBENZIDINE (3 3)

Explosive	Colour	Remarks
Blank	Faint blue tinge	J-acid soln identical action to conc H_2SO_4
Ammonium nitrate	Blue-violet	"
Ammonium perchlorate	As blank	"
Ammonium picrate	As blank	"
Black powder	Blue-violet	"
Dinitrobenzene	As blank	J-acid soln identical
Dinitrophenol	As blank	"
Dinitrotoluene	As blank	"
Dipicrylamine	As blank	"
Submarine blasting dynamite	Blue	"
Polar ammon gelatine dynamite	Blue	"
Ethylenediamine dinitrate	Blue-violet	"
Ethylenedinitramine	Blue-violet	J-acid soln gave green-brown
HMX	Blue-violet	J-acid soln gave blue flecks in spot
Picric acid	As blank	J-acid soln identical
PETN	Blue	"
RDX	Blue	J-acid soln gave blue flecks in spot
Sodium chlorate	Blue	J-acid soln gave blue edge to spot
Tetryl	Blue-violet	J-acid soln gave much slower colour
TNT	As blank	J-acid identical

TABLE 4

COLOUR REACTIONS OF EXPLOSIVES WITH VANADOUS SULPHATE (3 4)

Explosive	Colour	Remarks
Blank	Nil	
Ammonium nitrate	Blue-black	Colour permanent
Ammonium perchlorate	Deep blue flecks	Colour fades in ca 1 minute
Ammonium picrate	Nil	
Black powder	Deep blue	Colour permanent
Dinitrobenzene	Nil	
Dinitrophenol	Nil	
Dinitrotoluene	Nil	
Dipicrylamine	Nil	
Submarine blasting dynamite	Blue-black	Colour permanent
Polar ammon gelatine dynamite	Blue-black	Colour permanent
Ethylenediamine dinitrate	Blue-black	Colour permanent
Ethylenedinitramine	Deep blue flecks changing to greenish yellow	Greenish yellow colour permanent
HMX	Blue flecks changing to greenish yellow	Fades in ca 10 min leaving green tint
Picric acid	Nil	
PETN	Blue-black flecks	Colour permanent
RDX	Blue-black flecks	Colour permanent
Sodium chlorate	Deep blue	Colour permanent
Tetryl	Deep blue flecks fading to greenish yellow	Greenish yellow colour permanent
TNT	Nil	

TABLE 5

COLOUR REACTIONS OF EXPLOSIVES WITH THYMOL (3 5)

Explosive	Colour	Remarks
Blank	Brick red	J-acid soln identical action to conc H_2SO_4
Ammonium nitrate	As blank	"
Ammonium perchlorate	As blank	"
Ammonium picrate	As blank	"
Black powder	Green flecks	"
Dinitrobenzene	As blank	"
Dinitrophenol	As blank	"
Dinitrotoluene	As blank	"
Dipicrylamine	As blank	"
Submarine blasting dynamite	Deep green	J-acid soln gives yellow green
Polar ammon gelatine dynamite	Green tinge at edge	J-acid soln identical
Ethylenediamine dinitrate	Green flecks	"
Ethylenedinitramine	As blank	"
HMX	As blank	"
Picric acid	As blank	"
PETN	Greenish brown	"
RDX	As blank	"
Sodium chlorate	As blank	"
Tetryl	As blank	"
TNT	As blank	"

TABLE 6

COLOUR REACTION OF EXPLOSIVES WITH JANOVSKY REAGENT (4 6)

Explosive	Colour	Remarks
Blank	Nil	
Ammonium nitrate	Nil	
Ammonium perchlorate	Nil	
Ammonium picrate	Maroon	
Black powder	Nil	
Dinitrobenzene	Violet	Turns red-violet with time
Dinitrophenol	Intense yellow	
Dinitrotoluene	Transient blue	Turns dark brown
Dipicrylamine	Deep maroon	
Submarine blasting dynamite	Nil	
Polar ammon gelatine dynamite	Nil	
Ethylenediamine dinitrate	Nil	
Ethylenedinitramine	Nil	
HMX	Nil	
Picric acid	Maroon	
PETN	Nil	
RDX	Nil	
Sodium chlorate	Nil	
Tetryl	Maroon	
TNT	Reddish-violet	

TABLE 7

COLOUR REACTION OF EXPLOSIVES WITH J-ACID (3 7)

Explosive	Colour	Remarks
Blank	Nil	
Ammonium nitrate	Light brown	
Ammonium perchlorate	Nil	
Ammonium picrate	Nil	
Black powder	Light brown	
Dinitrobenzene	Nil	
Dinitrophenol	Nil	
Dinitrotoluene	Nil	
Dipicrylamine	Nil	
Submarine blasting dynamite	Faint brown	
Polar ammon gelatine dynamite	Light brown	
Ethylenediamine dinitrate	Reddish-brown	
Ethylenedinitramine	Yellow-brown	
HMX	Yellow-brown	
Picric acid	Nil	
PETN	Brown	
RDX	Yellow-brown	prior addn 1 drop DMF caused reddish-brown
Sodium chlorate	Reddish-brown	
Tetryl	Nil	
TNT	Nil	

With the exception of RDX noted, prior addition of 1 drop of either acetone or dimethylformamide did not improve the colour reaction; cyclohexanone gave a brown colour in the blank.

TABLE 8

COLOUR REACTION OF EXPLOSIVES WITH NESSLER'S REAGENT (3 8)

Explosive	Colour	Remarks
Blank	Nil	
Ammonium nitrate	Brown	
Ammonium perchlorate	Brown	
Ammonium picrate	Reddish brown	
Black powder	Nil	
Dinitrobenzene	Brown	Nitroaromatic reaction
Dinitrophenol	Yellow	" "
Dinitrotoluene	Yellow brown	" "
Dipicrylamine	Reddish brown	" "
Submarine blasting dynamite	Brown	
Polar ammon gelatine dynamite	Brown	
Ethylenediamine dinitrate	Nil	
Ethylenedinitramine	Nil	
HMX	Nil	
Picric acid	Brown	Nitroaromatic reaction
PETN	Nil	
RDX	Nil	
Sodium chlorate	Nil	
Tetryl	Reddish brown	Nitroaromatic reaction
TNT	Maroon	" "

TABLE 9

COLOUR REACTION OF EXPLOSIVES WITH DIPHENYLAMINE/CONC H_2SO_4 (3 9)

Explosive	Colour	Remarks
Blank	Nil	No colour after 3 min
Ammonium nitrate	Blue	
Ammonium perchlorate	Nil	
Ammonium picrate	Nil	
Black powder	Blue flecks	
Dinitrobenzene	Nil	
Dinitrophenol	Nil	
Dinitrotoluene	Nil	
Dipicrylamine	Nil	
Submarine blasting dynamite	Blue flecks	
Polar ammon gelatine dynamite	Blue flecks	
Ethylenediamine dinitrate	Blue flecks	
Ethylenedinitramine	Blue flecks	
HMX	Blue flecks	Colour develops in 1 min
Picric acid	Nil	
PETN	Blue flecks	
RDX	Blue	
Sodium chlorate	Blue	
Tetryl	Blue flecks	Colour develops slowly
TNT	Nil	

TABLE 10

COLOUR REACTION OF EXPLOSIVES WITH DIPHENYLAMINE/H_3PO_4 (3 10)

Explosive	Colour	Remarks
Blank	Nil	No colour after 10 min
Ammonium nitrate	Blue	
Ammonium perchlorate	Nil	
Ammonium picrate	Nil	
Black powder	Blue flecks	
Dinitrobenzene	Nil	
Dinitrophenol	Nil	
Dinitrotoluene	Nil	
Dipicrylamine	Nil	Prior addn of solvent gives orange which reagent discharges
Submarine blasting dynamite	Blue flecks	Colour took several minutes to form
Polar ammon gelatine dyhamite	Blue flecks	Colour slow to develop
Ethylenediamine dinitrate	Blue flecks	
Ethylenedinitramine	Nil	
HMX	Nil	
Picric acid	Nil	
PETN	Nil	
RDX	Nil	
Sodium chlorate	Blue flecks	
Tetryl	Nil	
TNT	Nil	

Prior addition of 1 drop of either acetone or dimethylformamide did not improve the colour reaction; cyclohexanone gave a faint brown colour to the blank.

TABLE 11

COLOUR REACTION OF EXPLOSIVES WITH GRIESS REAGENT (3 11)

Explosive	Colour	Remarks
Blank	Nil	No colour after 5 min
Ammonium nitrate	Red	
Ammonium perchlorate	Nil	
Ammonium picrate	Nil	
Black powder	Red	
Dinitrobenzene	Nil	
Dinitrophenol	Nil	
Dinitrotoluene	Nil	
Dipicrylamine	Nil	Solvents give orange colour, but reagent has no effect
Submarine blasting dynamite	Red flecks	
Polar ammon gelatine dynamite	Red	
Ethylenediamine dinitrate	Red edge	
Ethylenedinitramine	Red	
HMX	Nil	Prior addn of solvent causes reagent to give faint red edges
Picric acid	Nil	
PETN	Nil	Prior addn of solvent causes reagent to give faint red edges
RDX	Nil	" "
Sodium chlorate	Nil	
Tetryl	Red	Colour very slow to develop. Prior addn solvent speeded reaction
TNT	Nil	

Only in the cases noted did prior addition of 1 drop of acetone, cyclohexanone, or dimethylformamide enhance the colour development; even in these cases the reaction was so slow, and the colour so faint as to not constitute a positive field test.

TABLE 12

COLOUR REACTION OF EXPLOSIVE WITH FRANCHIMONT REAGENT (3 12)

Explosive	Colour	Remarks
Blank	Nil	
Ammonium nitrate	Violet-red	
Ammonium perchlorate	Nil	
Ammonium picrate	Nil	
Black powder	Violet-red	
Dinitrobenzene	Brown tint	Colour forms slowly ca 5 min
Dinitrophenol	Brown	Colour forms slowly ca 1 - 2 min
Dinitrotoluene	Violet tint	Colour forms slowly ca 2 min
Dipicrylamine	Reddish brown	Colour forms slowly ca 2 - 3 min
Submarine blasting dynamite	Violet-red	
Polar ammon gelatine dynamite	Violet-red	
Ethylenediamine dinitrate	Violet-red	
Ethylenedinitramine	Violet-red	
HMX	Violet-red	1 drop acetone required to dissolve HMX before test
Picric acid	Nil	
PETN	Violet-red	Colour forms in ca 1 min, reaction speeded up by addition of acetone
RDX	Violet-red	
Sodium chlorate	Nil	
Tetryl	Violet-red	Colour forms in ca $\frac{1}{2}$ min
TNT	Nil	

TABLE 13

COLOUR REACTION OF EXPLOSIVES WITH AZIDE/IODINE (4 13)

Explosives	Colour	Remarks
Blank	Nil	
Ammonium nitrate	Nil	
Ammonium perchlorate	Nil	
Ammonium picrate	Nil	
Black powder	Grey	Colour caused by micro-bubbles of gas
Ash from burnt black powder	Grey	Much greater gassing than above
Dinitrobenzene	Nil	
Dinitrophenol	Nil	
Dinitrotoluene	Nil	
Dipicrylamine	Nil	
Submarine blasting dynamite	Nil	
Polar ammon gelatine dynamite	Nil	Bubbles observable under microscope
Ethylenediamine dinitrate	Nil	
Ethylenedinitramine	Nil	
HMX	Nil	
PETN	Nil	
Picric acid	Nil	
RDX	Nil	
Sodium chlorate	Nil	
Tetryl	Nil	
TNT	Nil	

TABLE 14

COLOUR REACTION OF EXPLOSIVES WITH MANGANOUS SULPHATE (3 14)

Explosive	Colour	Remarks
Blank	Nil	
Ammonium nitrate	Nil	
Ammonium perchlorate	Nil	
Ammonium picrate	Nil	
Black powder	Nil	
Dinitrobenzene	Nil	
Dinitrophenol	Nil	
Dinitrotoluene	Nil	
Dipicrylamine	Nil	
Submarine blasting dynamite	Nil	
Polar ammon gelatine dynamite	Nil	
Ethylendiamine dinitrate	Nil	
Ethylenedinitramine	Nil	
HMX	Pink tinge	Colour develops when second reagent added
Picric acid	Nil	
PETN	Nil	
RDX	Nil	
Sodium chlorate	Red-violet	Addn of second reagent caused no change
Tetryl	Nil	
TNT	Nil	

TABLE 15

COLOUR REACTION OF EXPLOSIVES WITH SPAF (3 15)

Explosive	Colour	Remarks
Blank	Nil	Yellow tint from reagent
Ammonium nitrate	Nil	
Ammonium perchlorate	Nil	
Ammonium picrate	Nil	
Black powder	Nil	
Dinitrobenzene	Nil	
Dinitrophenol	Nil	
Dinitrotoluene	Nil	
Dipicrylamine	Nil	
Submarine blasting dynamite	Nil	
Polar ammon gelatine dynamite	Nil	
Ethylenediamine dinitrate	Nil	
Ethylenedinitramine	Dark Brown	
HMX	Nil	
Picric acid	Nil	
PETN	Nil	
RDX	Yellow-brown	
Sodium chlorate	Nil	
Tetryl	Brown	Possibly due to soly of CE in Me_2CO
TNT	Nil	

TABLE 16

COLOUR REACTION OF EXPLOSIVES WITH DIPHENYLAMINE/70% H_2SO_4 (3 16)

Explosive	Colour	Remarks
Blank	Nil	No colour after 5 min
Ammonium nitrate	Blue	
Ammonium perchlorate	Nil	
Ammonium picrate	Nil	
Black powder	Blue flecks	
Dinitrobenzene	Nil	
Dinitrophenol	Nil	
Dinitrotoluene	Nil	
Dipicrylamine	Nil	Solvents give orange, reagent has no effect
Submarine blasting dynamite	Blue flecks	
Polar ammon gelatine dynamite	Blue	
Ethylenediamine dinitrate	Blue flecks	
Ethylenedinitramine	Nil	
HMX	Nil	
Picric acid	Nil	
PETN	Blue flecks	
RDX	Blue flecks	Colour very slow in forming
Sodium chlorate	Blue	
Tetryl	Nil	
TNT	Nil	

Prior addition of 1 drop of acetone or dimethylformamide did not improve the colour reaction; cyclohexanone gave a brown colour with the blank.

TABLE 17

COLOUR REACTIONS OF EXPLOSIVES WITH CYANIDE REAGENT (3 17)

Explosive	Colour	Remarks
Blank	Nil	
Ammonium nitrate	Nil	
Ammonium perchlorate	Nil	
Ammonium picrate	Reddish brown	Colour forms slowly ca 2 min
Black powder	Nil	
Dinitrobenzene	Nil	
Dinitrophenol	Yellow	Colour turns reddish brown after ca 10 min
Dinitrotoluene	Nil	
Dipicrylamine	Reddish brown	
Submarine blasting dynamite	Nil	
Polar ammon gelatine dynamite	Nil	
Ethylenediamine dinitrate	Nil	
Ethylenedinitramine	Nil	
HMX	Nil	
Picric acid	Reddish brown	
PETN	Nil	
RDX	Nil	
Sodium chlorate	Nil	
Tetryl	Brown	Colour forms slowly ca 1 min
TNT	Reddish brown	Colour forms slowly ca 5 - 10 min

Note: The slow +ve reactions can be speeded up by the addition of a drop of ethanol to the spot.

TABLE 18

COLOUR REACTION OF EXPLOSIVES WITH ABPHSA (3 18)
AND WITH RIEGLER'S REAGENT (3 19)

Explosive	Reagent	Colour
Blank	ABPHSA	Reddish brown
All samples	"	As for blank
Blank	Riegler's	Yellow-brown
All samples	"	As for blank

TABLE 19

SUMMARY OF SPOT TESTS FOR EXPLOSIVES ON TAPE SUBSTRATE

Explosive	Colorimetric Test No																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
AN	-	-	+	+	-	-	+	+	+	+	+	+	-	-	-	+	-
AP	-	-	-	+	-	-	-	+	-	-	-	-	-	-	-	-	-
APc	+	-	-	-	-	+	-	+	-	-	-	-	-	-	-	-	+
BP	-	-	+	+	+	-	+	-	+	+	+	+	+	-	-	+	-
DNB	+	-	-	-	-	+	-	+	-	-	-	+	-	-	-	-	-
DNP	+	-	-	-	-	+	-	+	-	-	-	+	-	-	-	-	+
DNT	+	-	-	-	-	+	-	+	-	-	-	+	-	-	-	-	-
DPA	+	-	-	-	-	+	-	+	-	-	-	+	-	-	-	-	+
Dy/A	-	+	+	+	+	-	+	+	+	+	+	+	-	-	-	+	-
Dy/B	-	+	+	+	+	-	+	+	+	+	+	+	-	-	-	+	-
EDD	-	-	+	+	+	-	+	-	+	+	+	+	-	-	-	+	-
EDNA	-	-	+	+	-	-	+	-	+	-	+	+	-	-	+	-	-
HMX	-	-	+	+	-	-	+	-	+	-	-	+	-	+	-	-	-
PA	+	-	-	-	-	+	-	+	-	-	-	-	-	-	-	-	+
PETN	-	-	+	+	+	-	+	-	+	-	-	+	-	-	-	+	-
RDX	-	+	+	+	-	-	+	-	+	-	-	+	-	-	+	+	-
SC	-	+	+	+	-	-	+	-	+	+	-	-	-	+	-	+	-
CE	+	-	+	+	-	+	-	+	+	-	+	+	-	-	+	-	+
TNT	+	-	-	-	-	+	-	+	-	-	-	-	-	-	-	-	+

Reference should be made to the detailed tables (the numbers of which correlate with the test numbers) for fuller description of what constitutes a positive test.

Abbreviations: AN - ammonium nitrate, AP - ammonium perchlorate, APc - ammonium picrate, BP - Black powder, DNB - dinitrobenzene, DNP - dinitrophenol, DNT - dinitrotoluene, DPA - dipicrylamine, Dy/A - submarine blasting dynamite, Dy/B - polar ammon gelatine dynamite, EDD - ethylenediamine dinitrate, EDNA - ethylenedinitramine, HMX - octogen, PA - picric acid, PETN - pentaerythritol tetranitrate, RDX - hexogen, SC - sodium chlorate, CE - tetryl, TNT - trinitrotoluene

4 DISCUSSION

4 1 Detection and Characterization of Explosives

Identification and characterization of an explosive compound is a simple matter in the laboratory where modern equipment is available, although even there the complete characterization of all the constituents of an explosive mixture may be considerably more difficult. Jenkins and Yallop[3] have applied the elegant techniques of TLC to the identification of explosive residues, which may be only available in small amounts. However even this technique, with its minimum demands for expensive equipment, is felt to be inappropriate for field use.[4] Sophisticated equipment based on an electron capture detector head has been used under field conditions,[5] and an apparatus based on preliminary concentration and separation of vapours is under active development. Such equipment is expensive, and while when properly value engineered is suitable for use by non-scientists, is restricted in its applications to explosives that have an appreciable vapour pressure. The nitrate esters used in dynamite can readily be detected by such instruments, and it seems probable that TNT can also be detected. There remains a large number of compounds and mixtures that could be used as explosives, and for which no simple field test exists.

The American technique of using white adhesive tape as both the sampling device and also as the test reaction substrate offers a rapid and convenient method for screening both people and their environs for possible contamination with explosive substances.

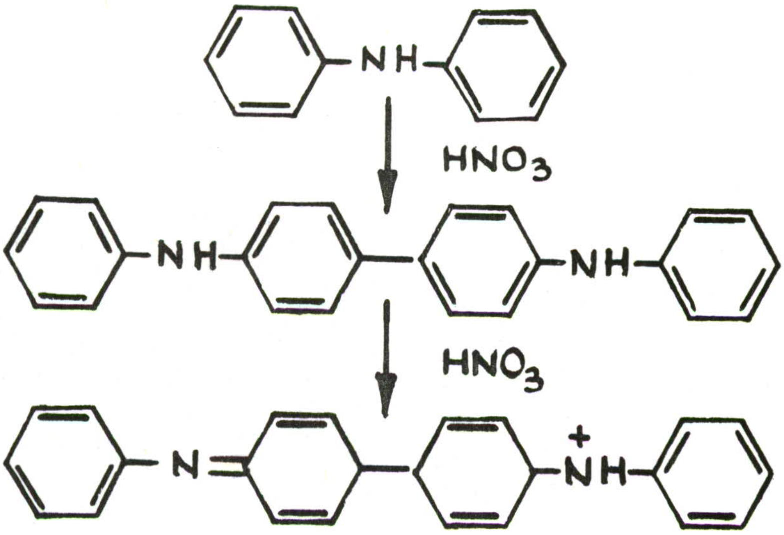
Unfortunately the tests reported to date are limited in that they are only claimed to apply to RDX and TNT, both explosives that have limited use in civil insurgency in the UK. The paucity of colorimetric tests for explosives is perhaps not surprising in view of the fact that explosive compounds are chosen on the basis (along with other characteristics) of their lack of reactivity.

We had available a series of colorimetric tests that had been developed for the identification of milligram quantities of explosives,[1,2] and we found that many of these tests could be adapted for use with the adhesive tape technique, the main limitation being that tests that required the application of heat were precluded.

4 2 Chemical Reactions of Explosives

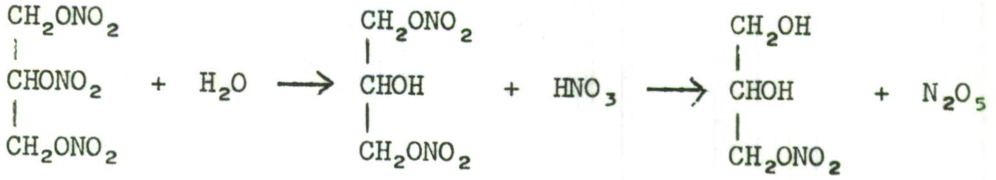
We have described elsewhere[6] the simple concept that a secondary explosive can be regarded as a fuel/oxidant mixture, the mixture being either at the molecular level, as in TNT, or at a mechanical level, as in black powder. This concept may be expressed better using chemical terminology, by saying that an explosive is a fuel/oxidant combination where the mode of combination may involve covalent bonds, ionic bonds, intermolecular forces, or any combination thereof. RDX and TNT are examples of covalently bonded explosives, guanidine nitrate and ethylenediamine dinitrate exemplify ionic explosives, and gelatine dynamites illustrate the synergy of physical effects with covalently bonded explosives.

In general explosives that use ionically bound oxidants are easy to detect, since the oxidant will dissolve and ionize in a suitable polar solvent, where it can then be reacted. Conversely such explosives may be very difficult to characterize since the number of ionic oxidants is limited, while the number of possible fuels is large. In practice most legitimate ionic explosives are based on nitrates, and the nitrate ion is readily detected by the oxidation of either diphenylamine or diphenylbenzidine in concentrated sulphuric acid to give intensely blue quinoidimonium salts.



The test is not specific for nitric acid, since other oxidants (nitrite, chlorate, peroxide, periodate, persulphate, and permanganate) also effect this reaction. Rather surprisingly perchlorate does not, neither does free perchloric acid.

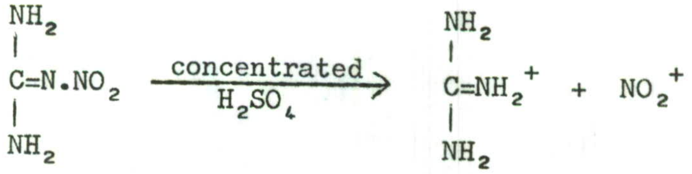
Nitrate esters occupy a mid point between ionic and covalently bound explosives. Thus, while the nitro group is covalently bound to the hydrocarbon skeleton by an ester oxygen, this bond is relatively easily hydrolyzed to produce free nitric acid. The hydrolysis is acid catalyzed, and the nitric acid produced may have only a formal existence, since it may be involved in further reaction to produce nitrogen oxides, as may be exemplified by the decomposition of nitroglycerine.



$$\begin{array}{l}CH_2ONO_2\\ |\\ CHONO_2\\ |\\ CH_2ONO_2\end{array} + H_2O \longrightarrow \begin{array}{l}CH_2ONO_2\\ |\\ CHOH\\ |\\ CH_2ONO_2\end{array} + HNO_3 \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2ONO_2\end{array} + N_2O_5$$

The exact mechanisms and final products of such decompositions in condensed systems do not concern us here; it is sufficient that in protonic solvents nitrate esters may be hydrolyzed to give nitrate ions that can be detected by the diphenylamine oxidation test.

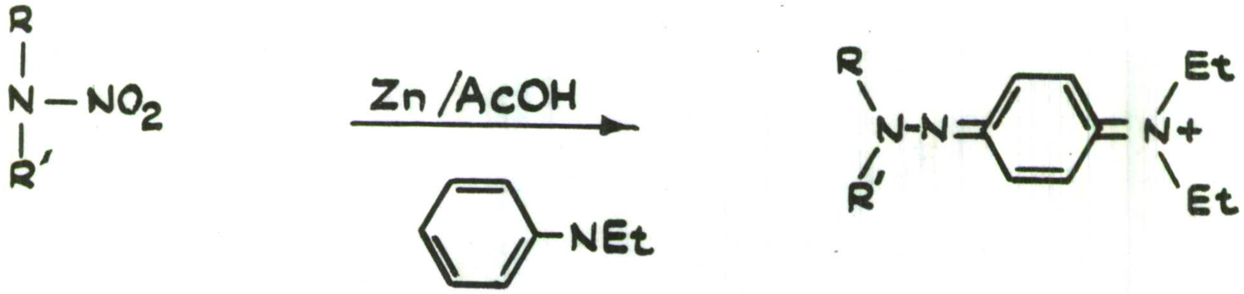
The nitrogen-nitrogen bond found in nitramines is stronger than the nitrogen-oxygen of nitrate esters and a similar type of hydrolysis does not occur. In solvents of sufficiently high acidity function protonation and ion exchange can occur, as is exemplified in the case of nitroguanidine.[7]



$$\begin{array}{l}NH_2\\ |\\ C{=}N.NO_2\\ |\\ NH_2\end{array} \xrightarrow[H_2SO_4]{\text{concentrated}} \begin{array}{l}NH_2\\ |\\ C{=}NH_2{}^+\\ |\\ NH_2\end{array} + NO_2{}^+$$

The nitronium ion thus produced acts as an oxidant, and thus nitramines may be detected by the diphenylamine oxidation test.

Nitramines may be more specifically detected by the Franchimont test[8] in which the nitramine group is reduced and then coupled with a suitable amine.



The exact mechanism of this reaction has not been unequivocally elucidated, but it seems probable that initial reduction of the nitramine to a nitrosohydroxyhydrazine induces coupling, possibly via intermediate C-nitrosation of the active para position of the aniline to give a highly coloured quinoidimonium salt.[9] The test is somewhat operator sensitive, but in the hands of experienced scientists[10] can be specific for certain nitramines. Nitrites interfere badly.

Nitrate salts, nitrate esters, and nitramines may all be subjected to alkaline reduction, and the ammonia thus liberated detected by the Nessler reagent. Amine cations such as ammonium,hydrazinium or guanidinium, will of course also react positively under such treatment.

The carbon-nitrogen bond, as exemplified in the aromatic nitro compounds, is the most stable found in explosophores, and there are no well authenticated colorimetric tests that detect such a subsituent group per se. The the polynitroaromatic system as a whole may be detected by the vivid colours they produce with alkali. This Janovsky test[11] was examined in detail by Amas and Yallop,[12] who describe reagents that have optimum sensitivity combined with ease of handling in the presence of certain alcohols, aldehydes or ketones. Amas and Yallop found that with their reagents dinitrotoluene gave a blue colour, and trinitrotoluene a red; nitroglycerine gave a slight yellow, and in the presence of dinitrotoluene this modified the final colour to green. The colours produced by various nitroaromatics, and by various aldehydic and ketonic reagents had earlier been comprehensively reviewed by Urbanski.[13]

In addition to the above general tests there are some that are specific for certain explosives. One of these is the well known thymol test for RDX described by Amas and Yallop;[14] the azide/iodine test is applicable to sulphur containing mixtures.[15]Feigel[15] also describes tests using potassium cyanide and sodium pentacyanoammine ferroate that give a variety of colours with nitroaromatics. The J-acid test as described to us was claimed to be specific for RDX.

4 3 Constraints of Field Testing

A major problem in devising field tests based on chemical reactions is to decide what are the appropriate limitations on equipment to be carried and techniques to be carried out. This investigation was made to determine what colorimetric spot tests were applicable to the adhesive tape sampling technique described by the Americans. Given the initial constraint that the tests were to be carried out on the sample on the tape substrate, we ruled out any prior solvent separation, such as one would initially attempt in a laboratory. The second constraint we imposed was that the experimental technique should only consist of the simple addition of drops of reagent (or small particles of solid if that were unavoidable), and that no physical treatment should be necessary. The third constraint was that the reactions involved should be effected at ambient temperature, thus ruling out some tests that depend upon heating. Electrolytic reactions were ruled out, although these would probably be fairly easy to achieve in the field. The final constraint was that the tests should give a result that could be interpreted by a trained non-scientist. In many ways this latter was the most severe constraint, since it meant that many of the subtle indications that colorimetric reactions afford the experienced analysts (cf Amas and Yallop[16]) had perforce to be discarded. A discussion of the suitability of the various tests subject to these constraints follows.

4 4 Colorimetric Spot Tests

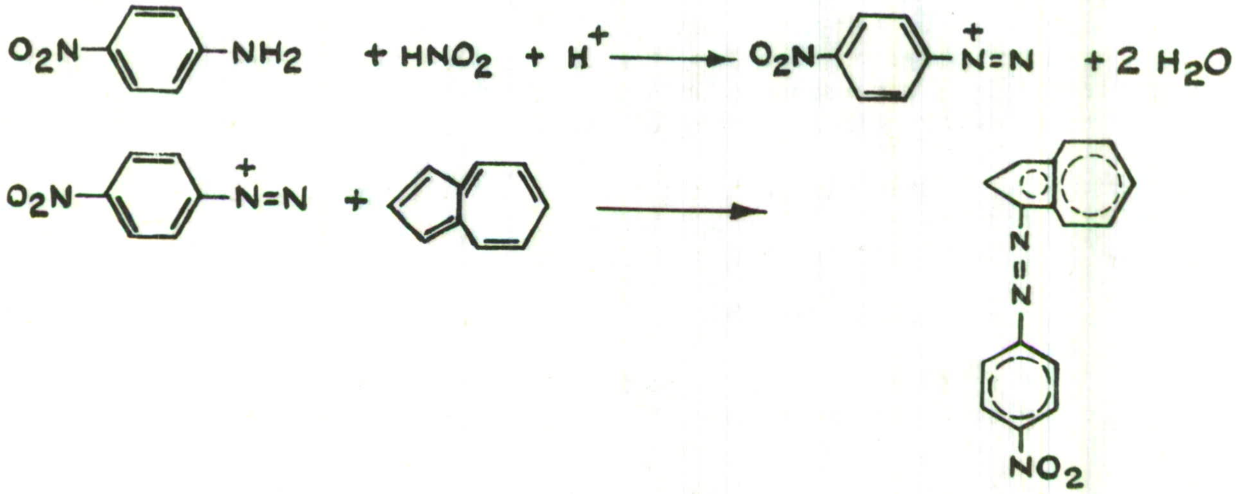
4 4 1 Alcoholic KOH Test

The reagent is easily prepared from stock chemicals, but the time required for complete solution of the potassium hydroxide is rather lengthy. A different reagent solution, made by dissolving the alkali in an equal weight of water and then adding 100 cm^3 of ethanol, was easier to prepare, and gave no significantly different reactions. The reagent had a relatively short shelf life (ca three weeks), turning orange on storage. The use of organic bases, as advocated by Amas and Yallop,[12] could well provide a better reagent, although the field supply position might be more difficult.

The reagent had no effect on the tape substrate, and could easily be applied dropwise at ambient temperature. Definite Meisenheimer type complexes, having very intense colours, were produced by dinitrotoluene, dipicrylamine, dinitrobenzene, and TNT. The dinitro compounds gave colours that had a blue element, although in the case of dinitrotoluene this was transient. The nitrophenols (picric acid, ammonium picrate, and dinitrophenol) gave yellow colours, and this is probably due to the formation of the coloured anion, and not to Meisenheimer complex formation. For the purpose of a field test by non-scientists these yellow colours were classed as a positive reaction along with the intense colours of the complexes.

4 4 2 Azulene Test

Azulene has been suggested as a coupling agent for the microdetermination of nitrite.[17]



Methods exist for the estimation of small amounts of nitroglycerine depending upon its alkaline hydrolysis to give nitrite,[18] and we decided to see if such hydrolysis could be detected by means of the azulene reagent. We found that nitroglycerine could be so detected, and also that RDX gave a similar reaction, whereas HMX did not. This difference in reactivity is explicable in terms of the known greater rate of alkaline hydrolysis of RDX as compared to HMX.[19] It seems probable that in terms of the azulene colour test this difference is more apparent than real, and that the overall governing factor is the solubility of the explosive in the solvent systems being used. Thus when only alcohol and acetic acid are present RDX gives a red-violet colour and HMX no colour. If a drop of acetone is added before the alcoholic potassium hydroxide, then RDX still gives the same red-violet colour, while HMX gives a yellow-green. Such clear distinctions between reactions of RDX and HMX are rare, and this constitutes a new and valuable distinctive test. If, however, a solution of HMX in acetone is treated with the azulene reagents, then the colour produced is identical with that given by RDX under similar conditions. It would thus seem that the difference in colour obtained when testing on a tape substrate is due to rate of solution, this effect possibly being enhanced by differences in rate of alkaline hydrolysis. The colour produced with sodium chlorate obviously depends upon a different mechanism; oxidation of the nitroaniline followed by coupling with the azulene would seem to be indicated.

The reagents are simple to prepare, although the shelf life of the azulene solution is brief. Addition of the reagents dropwise is simple, but care needs to be taken that the correct order is followed. There is no reaction with the tape substrate, but since the reagents themselves have a final faint blue colour, comparison with a blank is desirable. The positive reactions given by dynamite, RDX, HMX (if acetone is used) and sodium chlorate are clear and distinctive.

4 4 3 Diphenylbenzidine Test

The reagents are simple to prepare. Care must be taken to use a grade of sulphuric acid that is low in nitrate content, or else high blank values will be obtained. Analar reagent is just about satisfactory, Aristar is better. Care must be taken when handling the concentrated sulphuric acid. Nalge "one-drop" polythene bottles are suitable containers that non-scientists can handle safely. The reagents do not react with the tape substrate, but due care must be taken in disposing of the tape after test.

Of the compounds tested all that might be expected to give an ionizing species on concentrated sulphuric acid (with the exception of ammonium perchlorate) gave an intense and characteristic blue colour.

4 4 4 Vanadous Sulphate Test

In view of the failure to obtain a positive reaction with ammonium perchlorate in the diphenylbenzidine test some efforts were made to devise a modified test that would detect the perchlorate ion. Our approach was to reduce the perchlorate to chlorate, which would oxidize diphenylamine via diphenylbenzidine to the coloured quinoidimmonium cation. Freshly prepared hypovanadous sulphate was used as the reducing agent, and this was apparently successful since subsequent application of diphenylamine reagent gave the characteristic deep blue colour. However it seems doubtful if the concept of reduction to chlorate is the complete explanation, for the deep blue colour fades away after about one minute, whereas the colour produced by sodium chlorate under identical conditions is permanent. This permanence of colour, which is shown by most other compounds that can release an oxidant (with the exception of HMX, where a slow fading is observed, and EDNA) precludes the explanation that the hypovanadous sulphate is reducing the quinoidimmonium salt. A possible explanation is that the hypovanadous cation reduces the perchlorate to chlorate (which then oxidizes the diphenylamine), but in doing so is itself oxidized to a valence state that has the right reduction potential to reduce the quinoidimmonium salt. Since vanadium may have any valency from 2 to 5[20] this concept of successive reductions at different potentials has some possibility.

The reagents are troublesome to prepare, and involve both the toxic mercury and corrosive concentrated sulphuric acid; in default of any better tests for perchlorates this limitation must be accepted. Application of the reagents is simple, and the appearance of the characteristic blue colour, followed by a moderately rapid fading constitutes a fairly recognizable positive reaction for perchlorate. A skilled analyst might interpret the partial fading associated with HMX and EDNA, but for the non-scientist any permanent of near permanent colour should be taken as being negative.

4 4 5 Thymol Test

Amas and Yallop described the use of thymol to detect RDX,[14] and later amplified the experimental technique to permit of the detection of HMX.[16] The elegant procedure described by these skilled analysts permitted them to differentiate the similar coloured reactions produced by sugars and various aldehydes in this test. A few methylene nitramines and nitrosamines could also be detected. Unfortunately their technique requires heating the sample in concentrated sulphuric acid to temperatures up to 150°C, and so was not suitable for field use. We also found it difficult to obtain sulphuric acid that was sufficiently nitrogen-free that no colour was produced in a blank test. Bearing in mind our final constraint that the test should be applicable by non-scientists we concluded that a positive result could only be claimed where the colour produced was markedly different from that produced by a blank, and that mere differences in intensity must be disregarded. To our regret RDX was not distinguishable under our test conditions; we should emphasize that this failure should only be taken to reflect upon our chosen experimental conditions, and is in no respect a criticism of the thymol test itself.

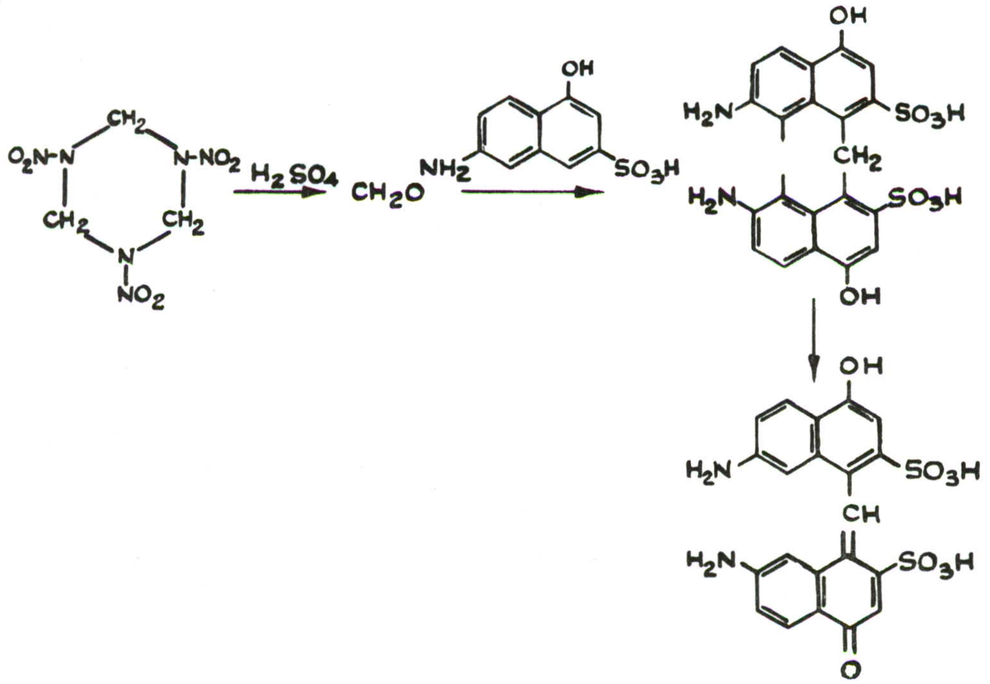
The thymol solution is easy to prepare; the concentrated sulphuric acid should be of the highest quality, standard analytical reagent grade giving a high blank colour, as did Aristar reagent. We found this interfering red colour of the blank also occurred when the test was conducted on a porcelain spot plate, although the colour did not develop as quickly as on the tape.

4 4 6 Janovsky Test

This is a variation of the alcoholic potassium hydroxide test, in which acetone is added to the tape substrate before the alkali reagent. While to some extent the acetone serves as a solvent, ensuing greater probability of reaction, its more important role lies in modifying the Meisenheimer complex produced by nitroaromatics. This effect is most noticeable in the case of the picrates, where maroon colours are produced rather than the mere enhancement of yellow that alcoholic potassium hydroxide alone produces. Dinitrobenzene and dinitrotoluene give blue complexes, but these are modified by time, and accordingly for the purposes of a field test no differential interpretation is suggested. The intense yellow given by dinitrophenol is considered as a positive reaction for field test purposes. The reagents are easy to prepare and to apply; some saving in manipulative time can be had by premixing the acetone with the alcoholic potassium hydroxide solution, but this results in a reagent with a much reduced shelf life (ca 2 days).

4 4 7 J-acid Test

As originally described this test was supposed to be specific for RDX, the only likely interferant being dried grass. The underlying chemistry was supposed to be dependant upon reaction of formaldehyde produced by the acid decomposition of the RDX.



We found that a number of the explosives tested gave a brown colour with J-acid (RDX gives a yellow-brown), and concluded that the test could not be specific for RDX. The compounds that produced this colouration all contain oxidant moities that give a positive diphenylamine test, and it would seem likely that oxidation is the basis of the colour reaction, rather than methylenation. The reagent is simple to prepare and to use, providing that the due precautions concerning concentrated sulphuric acid are observed.

4 4 8 Nessler's Test

The use of Nessler's reagent to detect ammonia by the precipitation of either black metallic mercury or the brown mercuric ammonium iodide $HgNH_2I.HgI_2$ is well known, and it would seem that this should offer a good method of detecting the ammonium cation in such explosives as ammonium nitrate, picrate or perchlorate. Unfortunately the reagent is alkaline, and this gives rise to colour production with nitroaromatics, which thus interfere. In the absence of alcohol or ketones these colours are not true Meisenheimer complexes, and may be no more than simple condensation products formed from the aci-salts; the yellows and browns produced are indistinguishable from the genuine brown precipitate of a positive Nessler's test as viewed for a field test. We also obtained a brown colour with the two types of dynamite tested; this may have been due to an ammonium salt present, or alternatively due to the reductive power of some organic species present.[15] The reagent is troublesome to prepare, but simple to apply to the tape substrate. For field test purposes the formation of a brown colour should be regarded as positive, but it is not specifically indicative of the presence of an ammonium salt.

4 4 9 Diphenylamine-I Test

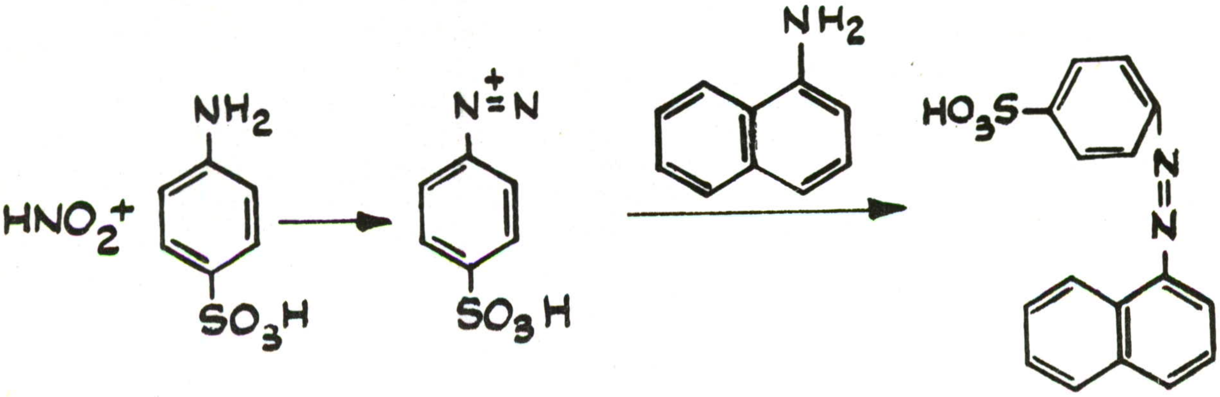
The chemistry of this reaction has been discussed above. The reagent is less sensitive than diphenylbenzidine, and the colour produced is sometimes a less pure blue. This suggests that in addition to the twofold loss in sensitivity suggested by the stoichiometry (the initial step being the oxidation of diphenylamine to diphenylbenzidine), there may be further losses due to side reactions. From the view point of a field test the loss in sensitivity may have the compensating advantage that a high incidence of positive blanks is avoided. The reagent is easy to prepare and use, but due precautions concerning concentrated sulphuric acid must be observed.

4 4 10 Diphenylamine-II Test

The diphenylamine or diphenylbenzidine tests depend upon the presence of an oxidizing species, and, as discussed above, this may arise from ionization (eg ammonium nitrate), hydrolysis (eg nitroglycerine) or heterolysis (eg RDX). The high acidity function of concentrated sulphuric acid ensures that all these reactions occur where possible. The use of a less acidic medium could cause some differentiation, in as much as the heterolysis reactions, which depend upon protonation, would be eliminated. Strong phosphoric acid (85%) is a medium which effects such a differentiation, the nitramines giving no reaction. There is indeed a further possible differentiation, in that the nitrate esters (as in the dynamites) hydrolyse much more slowly than in concentrated sulphuric acid, as evidenced by the slow formation of a blue colour. (PETN does not seem to hydrolyze at all.) Time-dependent reactions are not really suitable for field tests by non-scientists (some experienced analysts have been able to differentiate between various nitramines by careful choice of the acidic medium for this test[21]), and thus the appearance of a blue colour should be regarded as positive even if slow in formation. The reagent is simple to prepare and use; phosphoric acid, while still dangerous, is less corrosive than concentrated sulphuric acid.

4 4 11 Griess Test

This well known test for nitrites is dependent upon the nitrous acid forming a diazonium salt which then couples to give a red azo dyestuff.



While nitrites are not a common ingredient of explosives (although they could be used by amateurs) nitrates can be identified as nitrites following reduction. Feigl recommends acetic acid/zinc dust, but we found Devarda's alloy a more reproducible reducing agent. In addition to nitrates nitrate esters might be expected to give a Griess test providing that some degree of initial hydrolysis occurred. Nitroglycerine (as evidenced by the two dynamites) apparently does, but PETN does not. Given suitable conditions nitramines might also be expected to enter into this coupling reaction, which is similar to the Franchimont reaction (cf above). Ethylenedinitramine (EDNA) does, and tetryl does, although very slowly, but RDX and HMX do not. These results are what one would expect both on terms of the solubility of these nitramines and also of their reactivity. Prior addition of a solvent such as acetone or dimethylformamide enabled one to get a positive reaction from RDX, HMX and PETN, and speeded the response of tetryl. Since in the first three cases the extent of reaction was still only small, and since also dipicrylamine gave a colour due only to the solvent effect it was concluded that prior solvent addition had no advantages. The Griess reagent itself is somewhat troublesome to prepare; the addition of a speck of Devarda's alloy requires some degree of manipulative skill.

4 4 12 Franchimont Test

The chemistry of this well-known test for nitramines has been discussed above. As used in organic chemistry nitrites are the only common interferent, but our results would seem to suggest that this immunity is the result of the history of synthesis rather than of chemical specificity. Under the conditions used for tape substrate testing nitrates and nitrate esters both gave a positive reaction, which might be expected in view of the chemistry discussed in relation to the Griess test. More unexpected were the positive colour reactions obtained with the nitroaromatics. The slowness of response suggests that reduction of the relatively unreactive C-nitro groups is occurring, with subsequent coupling. This difference in reactivity between the Franchimont and Griess tests with respect to the nitroaromatics is attributable to the acidity and solvation power of the media used: glacial acetic acid as opposed to 30% aqueous acetic acid. Under the conditions used the Franchimont test may be regarded as lacking in specificity. The reagent is simple to prepare, but the addition of the Devarda's alloy requires some degree of manipulative skill.

4 4 13 Azide/iodine Test

The rate of reaction between sodium azide and iodine is markedly catalyzed by the presence of sulphides, thiosulphates and thiocyanates.[15]

$$\mathrm{NaS} + \mathrm{I_2} \longrightarrow \mathrm{INa{-}SI}$$

$$\mathrm{INa{-}SI} + 2\,\mathrm{NaN_3} \longrightarrow \mathrm{NaS} + 2\,\mathrm{NaI} + 3\,\mathrm{N_2}$$

While free sulphur itself does not catalyze this reaction, the sensitivity is such that one might expect to detect the traces of sulphides, etc that would be contained in explosives utilizing sulphur (eg black powder). The post-explosion residues of such materials would contain oxidized sulphur in the form of thiosulphates, thiocyanates, etc, and as such would be more detectable than the parent material. We found that black powder could be detected by the azide/iodine test, and that the residue from burnt black powder gave an even better response. The reagent is easy to prepare and use, but the actual response needs close observation, in as much as the initial release of the nitrogen manifests itself as the appearance of a grey colour in the brown solution. With time, or with greater concentrations of sulphide, discernable gas bubbles appear. A hand lens assists in the observation of this test.

4 4 14 Manganous Sulphate Test

A fairly specific test for chlorate depends upon the formation of complex manganese^{III} phosphate ions;[15] persulphates and periodates behave similarly.

$$ClO_3^- + 6\ Mn^{++} + 12\ PO_4^{\equiv} + 6\ H^+ \longrightarrow 6\ Mn(PO_4)_2^{\equiv} + Cl^- + 3\ H_2O$$

The colour of the complex manganese-containing anion is similar to that of the permanganate ion. Quantities of the complex anion too small to be detected by their colour can be discerned by adding diphenylcarbazide, when a violet colour results. The reagents are simple to prepare and to use, due precautions being taken over the handling of syrupy phosphoric acid. Sodium chlorate gave the expected reaction, as surprisingly did HMX (when diphenylcarbazide was added). We cannot advance any chemistry that would explain the HMX reaction, and suggest that it was probably due to advantitious contamination.

4 4 15 SPAF Test

Sodium pentacyanoammine ferroate has been used as a colorimetric reagent for nitramines, in particular for RDX. We found that we obtained a positive reaction with RDX and with EDNA, and possibly with tetryl (although the latter may have been due to solubility alone). In the past we have found this test to be very dependent upon the source and age of the reagent, and would not recommend it for field use.

4 4 16 Diphenylamine-III Test

As an alternative to the use of phosphoric acid as a less powerful acidic medium for the diphenylamine test 70% sulphuric acid was tried. This medium seemed to have a slightly greater ionizing effect, for RDX and PETN, neither of which gave reactions with the phosphoric acid reagent, gave positive results. The reagent is slightly more difficult to prepare than phosphoric acid, and more corrosive to handle.

4 4 17 Cyanide Test

Fiegl[15] suggests the use of alkaline sodium picrate as a colorimetric spot test for cyanide ions. We have found that this test may be reversed, and alkaline cyanide be used as a test for nitroaromatics. The reddish brown colour produced by this test is different from the Meisenheimer complex encountered in the alcoholic potassium hydroxide and Janovsky tests, and must involve a cyanide complex. All the trinitro aromatic compounds tested gave a positive reaction, but dinitrobenzene and dinitrotoluene did not. Dinitrophenol gave a yellow colour, which turned reddish-brown after about 10 minutes. The reactions are speeded by the prior addition of a drop of ethanol. The reagent is easy to prepare and use, but due precautions must be taken over the handling of a cyanide solution.

4 4 18 ABPHSA Test

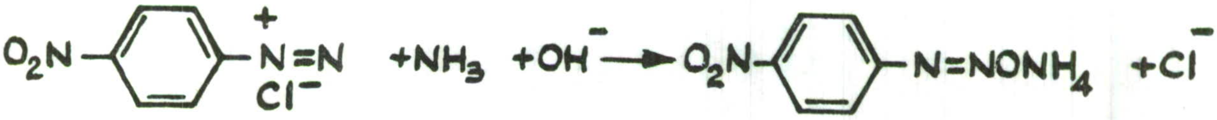
The aqueous solution of azobenzenephenylhydrazine sulphonic acid reacts with aldehydes giving deep red or blue solutions.[15]

This would seem to be a suitable test to detect formaldehyde if it were produced by acid hydrolysis of methylene nitramines such as RDX (cf chemistry of J-acid test). The reagent is difficult to obtain, requires the use of concentrated sulphuric acid, and under our conditions gave high blank values; we do not recommend it for field use.

4 4 19 Riegler's Test

This sensitive test for ammonia depends upon the red colouration produced when p-nitrobenzene diazonium chloride is mixed with a solution containing an ammonium salt and the whole then made alkaline.[15]

For spot test purposes solid calcium oxide offers a convenient method of introducing the appropriate amount of alkali.



The reagent is troublesome to prepare, and we obtained high blank values; we do not recommend the reaction for field test use.

4 5 Specific Identification Key

With the exception of ammonium perchlorate and sodium chlorate none of the explosives examined was identified uniquely by one specific test. It seems unlikely that a series of tests could be developed that would give unique tests for the other compounds. Nevertheless positive identification of a single compound is possible if a systematic scheme of testing is followed. Such a scheme is set out below, the operator being directed to the next appropriate test according to the results obtained. For the purposes of such a scheme tests are considered to have only either a positive or negative result (these being defined as in the experimental section), although the experienced operator would obviously derive some information from the exact nature of a positive result (cf Janovsky and diphenylamine-II tests). Indeed some qualitative interpretation is required to obtain final identification in the case of the nitroaromatics.

TABLE 20

FIELD TEST I (JANOVSKY TEST OR ALCOHOLIC KOH)

Test candidates: ammonium nitrate, ammonium perchlorate, ammonium picrate, Black powder, 1,3-dinitrobenzene, 2,4-dinitrophenol, 2,4-dinitrotoluene, dipicrylamine, Dynamite A (Submarine Blasting Dynamite), Dynamite B (Polar Ammon Gelatine Dynamite), ethylenediamine dinitrate, ethylenedinitramine, hexogen (RDX), octogen (HMX), pentaerythritol tetranitrate (PETN), picric acid, sodium chlorate, tetryl, trinitrotoluene	
Positive Result (Red, violet or yellow colour)	Negative Result (As for blank)
Ammonium picrate Dinitrobenzene Dinitrophenol Dinitrotoluene Dipicrylamine Picric acid Tetryl Trinitrotoluene	Ammonium nitrate Ammonium perchlorate Black powder Dynamite A Dynamite B Ethylenediamine dinitrate Ethylenedinitramine HMX PETN RDX Sodium chlorate
Go to Field Test II	Go to Field Test V

TABLE 21

FIELD TEST II (CYANIDE TEST)

<table>
<tr><td colspan="2">Test candidates: ammonium picrate, dinditrobenzene, dinitrophenol, dinitrotoluene, dipicrylamine, picric acid, tetryl, trinitrotoluene</td></tr>
<tr><th>Positive Result
(Reddish brown or yellow colour)</th><th>Negative Result
(As for blank)</th></tr>
<tr><td>Ammonium picrate
Dinitrophenol
Dipicrylamine
Picric acid
Tetryl
Trinitrotoluene
Go to Field Test III</td><td>Dinitrobenzene
Dinitrotoluene
(Not distinguishable by simple tape tests)</td></tr>
</table>

TABLE 22

FIELD TEST III (FRANCHIMONT TEST)

<table>
<tr><td colspan="2">Test candidates: ammonium picrate, dinitrophenol, dipicrylamine, picric acid, tetryl, trinitrotoluene</td></tr>
<tr><th>Positive Result
(Red, brown or violet colour)</th><th>Negative Result
(As for blank)</th></tr>
<tr><td>Dinitrophenol
Dipicrylamine
Tetryl
Go to Field Test IV</td><td>Ammonium picrate
Picric acid
Trinitrotoluene
(Picrates give yellow or orange with Field Test I - alcoholic KOH)</td></tr>
</table>

TABLE 23

FIELD TEST IV (DIPHENYLBENZIDINE OR DIPHENYLAMINE-I TEST)

Test candidates: dinitrophenol, dipicrylamine, tetryl	
Positive Result (Blue colour)	Negative Result (As for blank)
Tetryl	Dinitrophenol Dipicrylamine (Dinitrophenol gives yellow colour in Field Tests I and II)

TABLE 24

FIELD TEST V (AZULENE TEST)

Test candidates: ammonium nitrate, ammonium perchlorate, Black powder, Dynamite A, Dynamite B, ethylenediamine dinitrate, ethylenedinitramine, HMX, PETN, RDX, sodium chlorate	
Positive Result (Reddish violet or green colour)	Negative Result (As for blank)
Dynamite A Dynamite B RDX Sodium chlorate	Ammonium nitrate Ammonium perchlorate Black powder Ethylenediamine dinitrate Ethylenedinitramine HMX PETN
Go to Field Test VI	Go to Field Test VIII

TABLE 25

FIELD TEST VI (GRIESS TEST)

Test candidates: Dynamite A, Dynamite B, RDX, sodium chlorate	
Positive Result (Red colour)	Negative Result (As for blank)
Dynamite A Dynamite B (Not distinguishable by simple tape tests)	RDX Sodium chlorate Go to Field Test VII

TABLE 26

FIELD TEST VII (FRANCHIMONT TEST)

Test candidates: RDX, sodium chlorate	
Positive Result (Red or violet colour)	Negative Result (As for blank)
RDX	Sodium chlorate

TABLE 27

FIELD TEST VIII (DIPHENYLAMINE-II TEST)

Test candidates: ammonium nitrate, ammonium perchlorate, Black powder, ethylenediamine dinitrate, ethylenedinitramine, HMX, PETN	
Positive Result (Blue colour)	Negative Result (As for blank)
Ammonium nitrate Black powder Ethylenediamine dinitrate Go to Field Test IX	Ammonium perchlorate Ethylenedinitramine HMX PETN Go to Field Test XI

TABLE 28

FIELD TEST IX (NESSLER'S TEST)

Test candidates: ammonium nitrate, Black powder, ethylenediamine dinitrate	
Positive Result (Brown colour)	**Negative Result (As for blank)**
Ammonium nitrate	Black powder Ethylenediamine dinitrate Go to Field Test X

TABLE 29

FIELD TEST X (AZIDE/IODINE TEST)

Test candidates: Black powder, ethylenediamine dinitrate	
Positive Result (Grey colour, gas bubbles)	**Negative Result (As for blank)**
Black powder	Ethylenediamine dinitrate

TABLE 30

FIELD TEST XI (DIPHENYLAMINE-III TEST)

Test candidates: ammonium perchlorate, ethylenedinitramine, HMX, PETN	
Positive Result (Blue colour)	**Negative Result (As for blank)**
Ethylenedinitramine PETN Go to Field Test XII	Ammonium perchlorate HMX Go to Field Test XIII

TABLE 31

FIELD TEST XII (GRIESS TEST)

Test candidates: ethylenedinitramine, PETN	
Positive Result (Red colour)	Negative Result (As for blank)
Ethylenedinitramine	PETN

TABLE 32

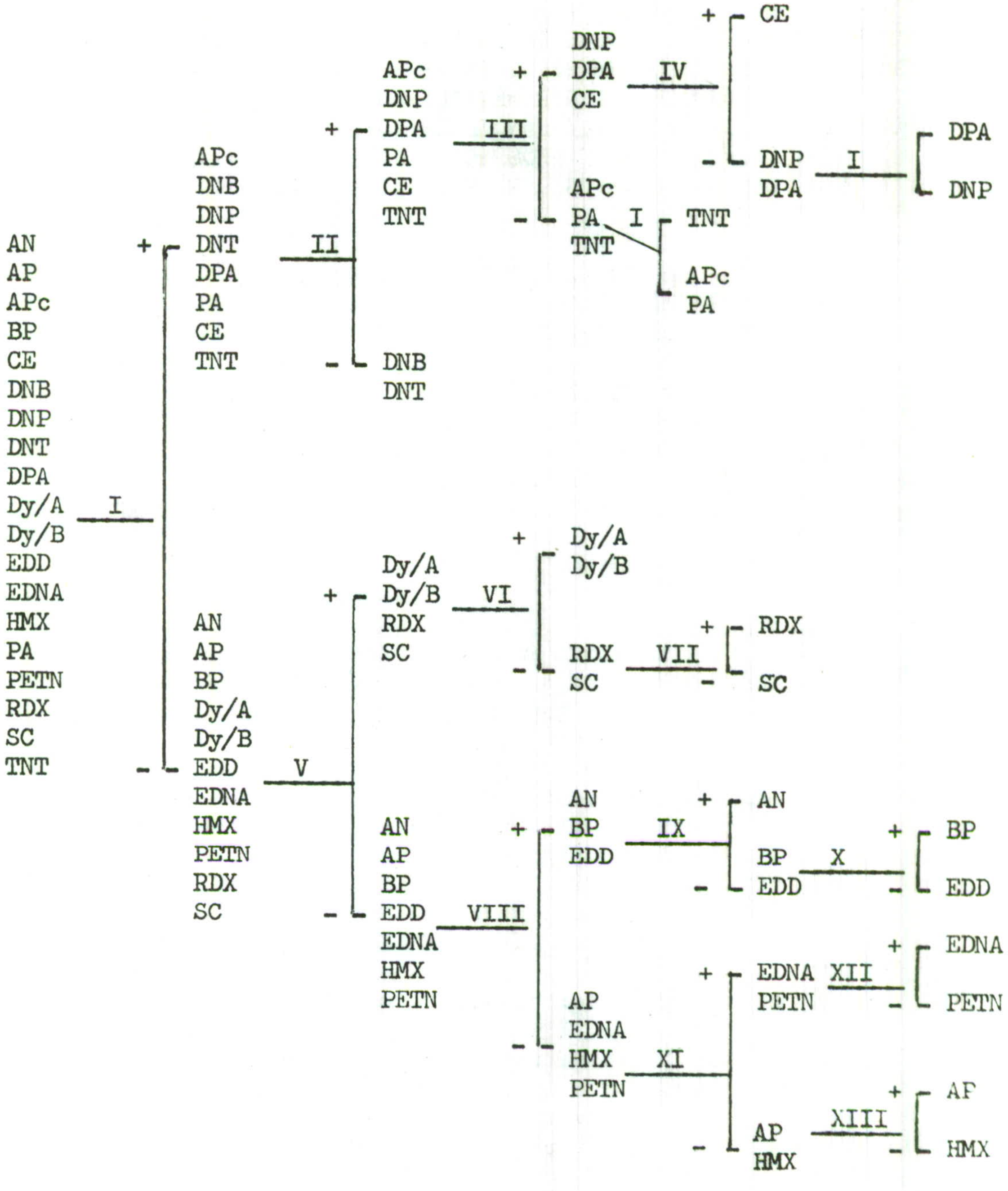
FIELD TEST XIII (NESSLER'S TEST)

Test candidates: ammonium perchlorate, HMX	
Positive Result (Brown colour)	Negative Result (As for blank)
Ammonium perchlorate (Confirm by vanadous sulphate test)	HMX

A flow diagram of this scheme of analysis is given below (abbreviations: AN - ammonium nitrate, AP - ammonium perchlorate, APc - ammonium picrate, BP - black powder, CE - tetryl, DNB - dinitrobenzene, DNP - dinitrophenol, DNT - dinitrotoluene, DPA - dipicrylamine, Dy/A - submarine blasting dynamite, Dy/B - polar ammon gelatine dynamite, EDD - ethylenediamine dinitrate, EDNA - ethylenedinitramine, HMX - octagen, PA - picric acid, PETN - pentaerythritol tetranitrate, RDX - hexogen, SC - sodium chlorate, TNT - trinitrotoluene).

This analytical scheme is accomplished using only ten tests (eleven if the confirmatory test for ammonium perchlorate is used; this is desirable since no positive test other than for ammonium ion has been obtained in arriving at this particular identification). Confirmatory tests strengthen the final identification: the results of all the tests tried are summarized in Table 1.

It should be emphasized that this analytical scheme is not unique, and that it has been constructed on the basis of only nineteen explosives. Obviously the scheme would become more complicated as more candidates were included, and further dimensions would be required to deal with explosive mixtures in which there were several constituents. Nevertheless this initial scheme indicates that a systematic classification is possible, and, most importantly, that only a limited number of tests and reagents are required, for the one test may be used several times (eg Franchimont test in Field Tests III and VII, Griess test in VI and XII).



(Roman numerals refer to Field Test)

4 6 Hazards

BECAUSE OF THE UNREACTIVE NATURE OF SOME EXPLOSIVES (THE METHYLENE NITRAMINES AND NITROAROMATICS IN PARTICULAR) IT IS NECESSARY TO EMPLOY POWERFUL REAGENTS FOR DETECTION REACTIONS. CONCENTRATED SULPHURIC ACID FEATURES IN MANY OF THE TESTS, AND THIS IS A NOTORIOUSLY DANGEROUS CHEMICAL. ALCOHOLIC ALKALI, GLACIAL ACETIC ACID, AND SYRUPY PHOSPHORIC ACID ARE ALSO CORROSIVE CHEMICALS, AND SOME OF THE ORGANIC REAGENTS USED HAVE TOXIC HAZARDS. THE TOXICITY OF CYANIDE SOLUTIONS SHOULD ALSO BE NOTED.

ALL THE REAGENTS DESCRIBED SHOULD BE HANDLED WITH PROPER CARE AND PRECAUTION. THEY PRESENT NO UNWARRANTED HAZARD TO THE EXPERIENCED CHEMIST, BUT DEFINITELY WOULD DO SO TO AN UNINSTRUCTED PERSON.

EQUALLY IMPORTANT IS THAT THE REAGENTS SHOULD ONLY BE APPLIED TO THE TRACES OF EXPLOSIVE THAT ARE GATHERED FOR TESTING BY AN ADHESIVE TAPE SUBSTRATE. UNDER NO CONDITIONS SHOULD THE REAGENTS BE APPLIED TO BULK SAMPLES OF EXPLOSIVES. THE ADDITION OF CONCENTRATED SULPHURIC ACID TO PERCHLORATE-BASED EXPLOSIVES, OR OF ALKALI TO ALUMINIUM-CONTAINING EXPLOSIVES COULD RESULT IN BULK DETONATION.

4 7 Scope

The purpose of this investigation was to determine whether some improvement could be made in the two colorimetric reactions that were originally described for use with adhesive tape sampling. We have demonstrated that considerable improvement is possible. The tests as originally described were intended for use by police officers. It is a matter for debate as to whether the extended range of tests we describe is suitable for such use. We have described the tests on the basis of a positive/negative response, and it would be possible to train a police officer to conduct the tests, and to interpret the results according to a proforma. Conclusions drawn under such conditions from a series of tests, the interpretation of which is subjective, can have only limited value. This may be sufficient to suggest a course of action on the spot; in no way should it be regarded as supplanting the role of the forensic scientist.

It could be argued that if field testing by a non-scientist has little forensic value then accurate and immediate identification of the explosive species in the field has relatively little importance: what is required is a test to determine whether an explosive is involved, full identification and characterization being left to the forensic scientist. All the explosives examined, with the exception of ammonium perchlorate, gave a positive response with either the Janovsky test or the diphenylamine test. Thus a simple field screening test can be based on these two tests. We have described field test kit based on these two tests, and the results of its application to a large range of explosives, in another report.[6]

5 CONCLUSIONS

5 1 Plastic white adhesive tape (3 M's 850) is a suitable substrate for colorimetric spot testing for explosives.

5 2 Many of the colorimetric tests for explosives that are normally carried out in glass can be made by spotting onto a tape substrate.

5 3 The technique is limited in that no physical separations are possible, and reactions must be done at ambient temperature.

5 4 Fine distinctions that are obvious to the experienced analyst working in a laboratory may be masked by the gross stoichiometry involved.

5 5 Even with these restrictions there remain a number of reactions which produce a marked colour reaction which can be interpreted on a positive/negative response basis.

5 6 An analytical scheme has been devised by which any one of nineteen typical explosives can be identified.

5 7 Further development would need to include the screening of a much larger range of explosives, and development of the reagents used for the specific conditions of testing on a tape substrate.

5 8 It would be possible to build a field test kit in which all necessary reagents were carried in polythene "one-drop" bottles.

5 9 Properly instructed non-scientists could operate such a kit for screening purposes; the value of such screening tests is a function of the subjectivity employed.

5 10 The forensic value of the full range of these tests as conducted by non-scientists would be limited; sufficient results can be obtained by applying only two of them (Janovsky test and diphenylamine-I test).

5 11 Many of the reagents are corrosive (in particular those based on concentrated sulphuric acid), and they may also be toxic or physiologically harmful. Proper precautions are due when handling them; they are not suitable for use by untrained personnel.

5 12 The tests are devised for traces of explosives as sampled by adhesive tape. Under no circumstances should the tests be applied directly to a bulk sample.

6 ACKNOWLEDGMENTS

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TEST

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Abstract Nineteen colorimetric spot tests performed on an adhesive tape substrate were examined and an analysis scheme devised to separate all the 19 representative explosives used in the investigation. Limited but adequate identification of most explosives was obtained using only two of the tests. New colorimetric tests were devised for RDX and HMX, and perchlorates, and the suitability of an existing test for cyanides for the detection of nitroaromatics exploited.

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Explosives Research and Development Establishment
THE IDENTIFICATION OF TRACES OF EXPLOSIVES BY FIELD SPOT TESTS
McDougall J L, Simkins R J J
March 1973
50 pp, 32 tabs, no figs

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Fort Belvoir, VA 22060-6218
U.S.A.

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