ENVIRONMENTAL SERVICES GROUP
REPORT NO. 2095/95

REPORT ON TRIALS CARRIED OUT TO EVALUATE THE HAZARDS OF EXPLOSIVELY CONTAMINATED TIMBER ROOFS

BRITISH AEROSPACE
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1. INTRODUCTION AND BACKGROUND

Royal Ordnance have been aware for a number of years that timber within buildings used for explosive processing has potential to absorb vapour of the explosive Nitroglycerine (NG). The possible non-destructive decontamination of such buildings as part of the remediation of the former RARDE site Waltham Abbey (North) has lead to a requirement to evaluate the hazard presented by NG contaminated timber to future occupiers of such buildings. The main use of timber in the buildings in question is for roofing boards.

During 1994, a significant number of samples from timber roofs to buildings at various locations were analysed for NG content. Results varied widely both between buildings, and within certain buildings. Building R603 at Royal Ordnance Waltham Abbey (South Site) was found to have an NG content of approximately 1.3 % in certain roof boards. Further tests on the distribution of NG within each board showed the greatest concentration to occur at the inner surface, a decrease with depth, and a possible rise on the outer surface. The distribution of concentrations within R603 was highly heterogenous, with 20 results varying between 1.3 mg/kg and 13245 mg/kg. (Note: the building is not compartmented). A summary of the R603 trials and results is attached at Appendix 2.

The levels of NG determined gave cause for concern that NG might be released from timber under certain environmental conditions which could cause a toxic risk to building occupants. To investigate this scenario, a phased experimental trial was commissioned, outlined at Appendix 1. In summary, Phase 1 would investigate the conditions under which NG would be released, Phase 2 would assess the effectiveness of certain treatments for NG contaminated timber, and Phase 3 would investigate flammability issues, and carry out longer term environmental tests on any treatment found to be effective. Phases 1 and 2 are now complete, and are reported on below. Certain aspects of Phase 3 are not now thought to be required. Longer term environmental trials are proceeding.

It is the assessment of Royal Ordnance Environmental Services Group that the levels of NG detected in timber roofs to date, or higher levels (up to say 10%) do not present any hazard of explosion.

2. EXPERIMENT DESCRIPTIONS AND RESULTS

2.1 PHASE 1

2.1.1 PHASE 1A : DETERMINATION OF OTHER POSSIBLE PRESENT ALIPHATIC NITRATE ESTERS.

In addition to NG, timber could also absorb certain other aliphatic nitrate esters which might be present. During previous timber analysis, certain unidentified peaks were obtained which might relate to wood resins, or might indicate an explosive related material. Samples of other aliphatic nitrate esters were obtained, namely: Glycerol-1-mononitrate, 1,2,-Dinitroglycerine and 1,3-Dinitroglycerine. Solutions of

these nitrate esters were prepared in acetone and compared with chromatograms obtained during the routine analysis of wood samples from Waltham Abbey North Site in an attempt to identify any of the 'unknown' peaks observed during the evaluation of results.

Results:

A poor chromatogram was obtained from the supplied 1,2-Dinitroglycerine due to impurities making identification difficult. It was decided not to use the supplied material for identification purposes.

Chromatograms obtained are shown at Appendix 4.

2.1.2 PHASE 1B : TO DETERMINE THE AFFINITY OF NITROGLYCERINE TO A WOODEN MATRIX.

Apparatus - The apparatus for the following experimental work was assembled as shown in Appendix 3.

Phase 1.b.1 ***To Determine an Effective Method of Trapping any Desorbed Aliphatic Nitrate Esters.***

It was decided to employ 'Waters Porapak RDX' solid phase extraction cartridges (See Appendix 5 for technical details) as a trapping medium. Three Porapak cartridges were connected in series using PTFE tubing.

Approximately 5 mg of Nitroglycerine was placed in a DSC weighing pan and transferred to the desorption vessel. The oven temperature was maintained at 50°C for the duration of the test.

The surrounding air from the desorption vessel was drawn through the Porapak cartridges at approximately 0.5 litre/min for 5 hours using a millipore oil-less vacuum pump.

The Porapak cartridges were then eluted into separate 10 ml volumetric flasks with approximately 8 ml of acetone and made up to the mark with acetone.

The eluents from the second and third cartridges were then analysed by gas chromatography using a TEA (Thermal Energy Analyser) detector against a 0.15 mg/L each EGDN/NG standard (EGDN is Nitroglycol, a similar explosive to NG) in acetone to determine the effectiveness of the selected trapping medium.

Results:

Nitroglycerine was found to be present in the eluent from the second Porapak (at trace level) whereas no Nitroglycerine was detected in the third Porapak eluent. The estimated detection limit for NG in these experiments is 0.01 mg/L.

Phase 1.b.2 ***To Determine if Quantification of any Desorbed Aliphatic Nitrate Ester is Possible.***

200 µL of a 15 mg/L each EGDN/NG standard in acetone (3×10^{-3} mg) were transferred to an evaporating basin which was then placed inside the desorption vessel.

The oven temperature was maintained at 50°C for the duration of the test.

The surrounding air from the desorption vessel was drawn through the Porapak cartridges at 0.5 litre/min for 3.5 hours.

The Porapak cartridges were then eluted as before into 10 ml volumetric flasks and analysed by gas chromatography using a TEA detector against a 0.15mg/L each EGDN/NG standard in acetone.

NOTE : The wood samples used for the following series of tests were obtained from Waltham Abbey South Site, Building R603 (Approx. sizes 150 mm x 50 mm x 50 mm), and consisted of sawn sections from the roof of that building, with no existing surface finishes. 17 samples, identified A - Q were prepared (not all were used).

All wood samples used in Phases 1 and 2 were kept for subsequent analysis.

Results:

3.00×10^{-3} mg of Nitroglycerine was placed in the DSC pan and thermally desorbed. 3.36×10^{-3} mg of Nitroglycerine was recovered from the first Porapak. No Nitroglycerine was detected in the second Porapak.

Recovery from the system was found to be 112%. This shows 100% recovery within the bounds of experimental error.

Phase 1.b.3 ***To Determine if Nitroglycerine can be Thermally Desorbed from Wood at 50°C.***

(Plank A)

The wood sample was placed in the desorption chamber. The oven temperature was maintained at 50°C whilst the surrounding air from the desorption chamber was drawn through the Porapak cartridges at a flow rate of 1.0 litre/min for a recorded period of time (6 hours).

The Porapak cartridges were then eluted as before into 10 ml volumetric flasks. The first Porapak cartridge eluent was analysed by RP-HPLC (Reverse Phase High Performance Liquid Chromatography) with Ultra Violet (UV) detection against a 50 mg/L mixed explosive standard in acetonitrile. The second Porapak cartridge eluent was analysed by gas chromatography using a TEA (Thermal Energy Analysis) detector against a 0.15 mg/L each EGDN/NG standard in acetone to determine if any breakthrough of analyte had occurred from the first cartridge.

It was decided to express results of desorbed Nitroglycerine from wood as a concentration in the extracted surrounding air so that a comparison could be made with the Occupational Exposure Limit (OEL) for Nitroglycerine in air which is currently 2 mg m^{-3}. This is discussed in detail in Section 5.

Results:

Sample Ref.	Porapak Position	Conc^{n} of NG. in Porapak eluent (mg l^{-1})	Volume of Air Sampled (Litres)	Conc^{n} of NG. in Air (mg m^{-3})	Conc^{n} of NG. in Sample after Desorption (mg kg^{-1})
Plank A	First	63.9	360	1.8	1519
Plank A	Second	N.D.	-	-	-

Phase 1.b.4 ***To Determine if Nitroglycerine can be Thermally Desorbed from Wood at 30°C.***

(Planks B & C)

The test as described in 1.b.3. above was repeated with the oven temperature maintained at 30°C.

The Porapak cartridges were eluted as before into 10 ml volumetric flasks. The first Porapak cartridge eluent was analysed by RP-HPLC with UV detection against a 15mg/L each EGDN/NG standard in acetone. The second Porapak cartridge eluent was analysed by gas chromatography using a TEA detector against a 0.15mg/L each EGDN/NG standard in acetone to determine if any breakthrough of analyte had occurred.

The above test was carried out in duplicate.

Results:

Sample Ref.	Porapak Position	Conc^{n} of NG. in Porapak eluent (mg l^{-1})	Volume of Air Sampled (Litres)	Conc^{n} of NG. in Air (mg m^{-3})	Conc^{n} of NG. in Sample after Desorption (mg kg^{-1})
Plank B	First	6.0	325	0.18	904
Plank B	Second	N.D.	-	-	-
Plank C	First	3.7	435	0.08	288
Plank C	Second	< 0.01	-	-	-

2.1.3 PHASE 1C : TEST TO EVALUATE THE EFFECT OF WATER PENETRATION ON NITROGLYCERINE CONTAMINATED WOOD.

Four pieces of wood (Planks L, M, N & O.) were weighed and placed in an extraction bottle. Three times this weight of water was then added to each of the bottles, lids replaced and the bottles placed on a reciprocal shaker for one week.

The water extract was then analysed by RP-HPLC with UV detection against a 15mg/L each EGDN/NG standard in acetone diluted 50:50 with water.

Results:

Sample Ref.	Conc^{n} of NG. (water extractable) in Wood Sample (mg kg^{-1})
Plank L	13.1
Plank M	139
Plank N	189
Plank O	156

After evaluation of the results from Phase 1, it was decided to proceed to Phase 2 - neutralisation/encapsulation.

2.2 PHASE 2

2.2.1 WOOD SAMPLE PREPARATION

Two pieces of wood were coated with polyurethane varnish in an attempt to encapsulate the wood (Planks D & E).

To attempt to neutralise the Nitroglycerine, separate 10% solutions of 0.880 ammonia and acetic acid (glacial form) in acetone were prepared. Acetone was used to aid penetration of the solutions into the wood, and ammonia and acetic acid because they offer the best prospect of degrading NG without introducing a further toxic hazard.

Two pieces of wood were sprayed with the prepared ammonia solution (Planks I & J). Two pieces of wood were sprayed with the prepared acetic acid solution (Planks F & G).

The prepared samples were then placed in a covered outbuilding for 1 week to allow for any neutralisation reactions to take place, and in the case of the polyurethane varnished sample, to allow any possible permeation of Nitroglycerine to the surface to occur.

Two untreated wood samples were also placed in the outbuilding as control samples (Planks H & K).

Two pieces of wood were painted with one coat of aluminium wood primer (Crown), one coat of an oil based undercoat (Dulux brilliant white) followed by a commercial fire retardant emulsion ('Quelfire'. This product is intumescent).

The painted samples were then allowed to stand in a heated section of the laboratory for 1 week to allow possible permeation of Nitroglycerine to occur (Planks P & Q).

2.2.2 PHASE 2A: DESORPTION OF POLYURETHANE COATED SAMPLE (PLANKS D & E).

The coated wood sample was desorbed as per phase 1.b at a temperature of 30°C.

The Porapak cartridges were eluted into 10 ml volumetric flasks with acetone. The first Porapak cartridge eluent was analysed by gas chromatography using a TEA detector against a 0.15 mg/L each EGDN/NG standard in acetone. The second Porapak cartridge eluent was also analysed by gas chromatography to determine if any breakthrough of analyte had occurred.

Results:

Sample Ref.	Porapak Position	Conc^{n} of NG. in Porapak eluent (mg l^{-1})	Volume of Air Sampled (Litres)	Conc^{n} of NG. in Air (mg m^{-3})	Conc^{n} of NG. in Sample after Desorption (mg kg^{-1})
Plank D	First	4.0	445	0.09	655
Plank D	Second	N.D.	-	-	-
Plank E	First	0.18	392	0.01	83.7
Plank E	Second	< 0.01	-	-	-

2.2.3 PHASE 2B: DESORPTION OF 10% ACETIC ACID/ACETONE TREATED WOOD SAMPLE (PLANK F)

The treated wood sample was desorbed at a temperature of 30°C.

The Porapak cartridges were eluted into 10 ml volumetric flasks with acetone. The first Porapak cartridge eluent was analysed by RP-HPLC with UV detection against a 15mg/L each EGDN/NG standard in acetone. The second Porapak cartridge eluent was analysed by gas chromatography using a TEA detector to determine if any breakthrough of analyte had occurred.

Results:

Sample Ref.	Porapak Position	Conc^{n} of NG. in Porapak eluent (mg l^{-1})	Volume of Air Sampled (Litres)	Conc^{n} of NG. in Air (mg m^{-3})	Conc^{n} of NG. in Sample after Desorption (mg kg^{-1})
Plank F	First	3.48	340	0.1	461
Plank F	Second	N.D.	-	-	-

Because it was clear from this result that the treatment had been un-successful in neutralising the NG, the second sample (Plank G), and the control (Plank H) were not processed.

2.2.4 PHASE 2C: DESORBTION OF 10% AMMONIA/ACETONE TREATED WOOD SAMPLE (PLANK I).

The treated wood sample was desorbed at a temperature of 30°C.

The Porapak cartridges were eluted into 10 ml volumetric flasks with acetone. The first Porapak cartridge eluent was analysed by RP-HPLC with UV detection against a 15mg/L each EGDN/NG standard in acetone. The second Porapak cartridge eluent was analysed by gas chromatography using a TEA detector to determine if any breakthrough of analyte had occurred.

Results:

Sample Ref.	Porapak Position	Conc^{n} of NG. in Porapak eluent (mg l^{-1})	Volume of Air Sampled (Litres)	Conc^{n} of NG. in Air (mg m^{-3})	Conc^{n} of NG. in Sample @ desorption (mg kg^{-1})
Plank I	First	1.93	495	0.04	409
Plank I	Second	N.D.	-	-	-

Because it was clear from this result that the treatment had been un-successful in neutralising the NG, the second sample (Plank J), and the control (Plank K) were not processed.

2.2.5 PHASE 2D: DESORPTION OF PAINTED WOOD SAMPLE (PLANKS P &Q).

The coated wood sample was desorbed at a temperature of 30°C.

The Porapak cartridges were eluted into 10 ml volumetric flasks with acetone. The first Porapak cartridge eluent was analysed by gas chromatography using a TEA detector against a 1.5 mg/L each EGDN/NG standard in acetone. The second Porapak cartridge eluent was also analysed by gas chromatography to determine if any breakthrough of analyte had occurred.

Results:

Sample Ref.	Porapak Position	Conc^{n} of NG. in Porapak eluent (mg l^{-1})	Volume of Air Sampled (Litres)	Conc^{n} of NG. in Air (mg m^{-3})	Conc^{n} of NG. in Sample @ desorption (mg kg^{-1})
Plank P	First	0.37	385	0.01	8328
Plank P	Second	N.D.	-	-	-
Plank Q	First	0.02	439	< 0.01	144
Plank Q	Second	N.D	-	-	-

2.2.6 EXTRACTION OF WOOD SAMPLES AFTER DESORPTION

In order to ascertain the approximate content of Nitroglycerine in each original sample, less the amount of Nitroglycerine that had been thermally desorbed, the desorbed wood samples from phases 1 & 2 were then weighed and extracted with three times their weight with acetone by volume overnight. The samples which had their surfaces coated as part of these tests were deeply scored with a sharp knife prior to extraction to break through the coated surfaces. Samples were then analysed by RP-HPLC with UV detection against a mixed explosive standard in acetonitrile. If no Nitroglycerine was detected by HPLC, then the extract was subsequently analysed by gas chromatography using a TEA detector against a 1.5 mg/L each EGDN/NG standard in acetone.

The results for each plank are listed with the experimental results above.

3. DISCUSSION OF RESULTS

When retention data for Glycerol-1-mononitrate, 1,3-Dinitroglycerol were compared with a typical wood sample extract from Waltham Abbey North Site, work to date identifies glycerol-1-mononitrate and 1,3-Dinitroglycerol as being present in typical extracts, with a tentative identification for one other 'unknown' peak as Glycerol-2-mononitrate.

It was confirmed through tests 1.b.1 and 1.b.2 that Porapak cartridges were suitable for the trapping and subsequent quantitative analysis of any possible desorbed aliphatic nitrate esters.

Upon thermally desorbing wood at 50°C it was found that the generated concentration of Nitroglycerine in air was 1.80 mg m^{-3}, which is approaching the occupational exposure limit of 2.0 mg m^{-3}. This data is related back to 'real' worst case building scenarios in Section 5.

As ambient temperatures would not normally expected to achieve 50°C, it was decided to carry out the desorptions at 30°C as this is a more probable ambient temperature.

Upon desorbing wood samples at 30°C, greatly differing results of Nitroglycerine concentration in air of 0.18 and 0.08 mg m^{-3} were obtained from the samples tested. This can possibly be explained by the fact that on analysis of the wood sample which gave the highest concentration of Nitroglycerine in air (Plank B), the sample was found to contain more than three times the concentration of Nitroglycerine found in the other sample (Plank C).

Upon examination of the results from the water displacement trial (test 1.b.5), it was found that water can displace high levels of nitroglycerine from a wood matrix.

From the results obtained from phase 1 tests, it was found that Nitroglycerine can be easily desorbed from a wood matrix. It was decided to carry out the tests outlined in phase 2.

It was found that a lower concentration of Nitroglycerine in air could be produced from samples coated with polyurethane varnish (Phase 2A), when compared to un-coated samples. It was again observed that the higher Nitroglycerine concentration in the wood sample gave a higher concentration of Nitroglycerine in air when thermally desorbed.

If more than one coat is applied, polyurethane varnish may seal the surface, but when it is subjected to fluctuating temperatures it is susceptible to cracking and flaking. This would then allow Nitroglycerine to be released from any exposed wood surfaces.

Attempts were made to neutralise any Nitroglycerine with acetic acid and ammonia solutions in acetone (Phase 2B & 2C). 10% solutions were chosen as this is the maximum concentration permissible of acetic acid or ammonia solution before they are classed by regulations as irritants. Acetone was chosen as the solvent for the above solutions to facilitate penetration of the solutions into the wood matrix. It was found that the acetic acid solution had little or no effect on the desorbed concentration of Nitroglycerine in air when compared to untreated wood samples. eg. Untreated wood (Plank B) produced a concentration of Nitroglycerine in air of 0.18 mg m^{-3} from a wood sample containing 904 mg kg^{-1} of Nitroglycerine. The acetic acid treated sample (Plank F) produced a concentration of Nitroglycerine in air of 0.10 mg m^{-3} from a wood sample containing 461 mg kg^{-1} , this difference probably being due to the original concentration of Nitroglycerine in the wood sample. Slightly better results were obtained with the ammonia solution, but again, total neutralisation did not occur.

It must be borne in mind that these tests were carried out under laboratory conditions where the samples were given a 'good soaking' in the chosen solution whereas, if the exercise were carried out on building structures, then a garden type sprayer would probably be employed and complete coverage of accessible areas could not be guaranteed. Also there is the issue of flammability risks when using acetone. The practicalities of the above techniques deem the above methods unsuitable.

In the case of the painted wood samples (Phase 2D), a very low concentration of Nitroglycerine in air was obtained ie. 0.01 mg m^{-3} from a wood sample with a Nitroglycerine in wood concentration of 8328 mg kg^{-1} .

In order to determine if, after a longer period of time, Nitroglycerine will permeate through the paint layers enabling it to desorb from the surface, a further four samples have been prepared and are being stored in a heated laboratory environment. It is intended that these samples be subjected to desorption trials after a period of three months to determine any possible changes.

4. HAZARD ASSESSMENT FOR RE-USE OF BUILDINGS

The question of the likelihood of NG contamination of wooden surfaces within a building resulting in levels above the HSE recommended exposure threshold of 2 mg m^{-3} can be examined. Taking a typical incorporator house bay at Waltham Abbey North Site, and average to bad conditions: *[The highest NG wood sample result from North Site is 186 mg/kg, although up to 13,000 mg/kg was obtained in R603 at South Site. The wide range of results obtained within R603 (4 orders of magnitude) indicates that sentencing roofs based on sparse sampling results should not be attempted.]*

Assumptions

Volume of room:	184 m^3
Area of timber roof:	55 m^2
Thickness of roof boards:	35 mm
Density of timber:	600 kg/m^3
Average NG content:	0.1% (1000 mg/kg)
No. of air changes per hour:	1*

**Note: actual number of air changes per hour is likely to be higher - 3 is normal*

Derived figures

Total weight of wood:	1155 kg
Total weight of NG:	1.155 kg

% release required to exceed 2 mg/m^3 threshold in 1 hour:

(2 x 184)/(1.155 x 10^6) = 0.032 % per hour.

Actual emission rate at 30° C from trial 1.b.4 (sample contained 904 mg/kg, sample weight was 100 grams):

(0.325 m^3 x 0.18 mg m^{-3} / 5.4 hours) / (904 mg kg^{-1} x 0.1 kg) = 0.012 % per hour.

Thus, the trial conditions (30° C, steady air flow over surface) duplicated within an Incorporator building on North Site would produce less than half the HSE recommended maximum threshold.

This indicates that there is probably not a toxic threat, given a maximum concentration of 1000 mg/kg of NG in roof boards. However, the factor of safety is not large, and there are indications from trial 1.b.5 that water may increase the desorption of NG into room air spaces, given typical leaking roofs. It is also clear that explosive buildings can have as much as 1% NG in some roof boards, whilst samples from other boards in the same room have only 0.0001 %. At the 1% level the risk of exceeding the occupational exposure threshold would seem to be high.

However, if the calculation is repeated using the result from Phase 2D (plank P) (painted with fire retardant), the release rate determined is 0.00007 % per hour. This release rate is two orders of magnitude lower, and should not result in the OEL being exceeded.

These calculations are only indicative, since there is no evidence that the NG release rate is linear with concentration.

5. CONCLUSIONS AND RECOMMENDATIONS

The analysis carried out in Section 5 indicates that HSE occupational exposure limits (OEL) for Nitroglycerine are unlikely to be exceeded under normal conditions within the incorporator buildings at Waltham Abbey North Site, assuming that the sample results obtained are representative. However, this conclusion is based on only two desorption experimental results. It is likely that the variable nature of timber, and also the local NG concentration, will affect release rates. Any draft proofing of rooms which reduced the number of air changes per hour would also affect the conclusion.

It is considered that the margin of safety based on the calculations carried out and the experimental results determined is insufficient to enable a confident assertion that the OEL will never be exceeded. The results of the experiments to treat wood with materials to degrade NG were poor, and this cannot be recommended as a solution. However, the encapsulation of the NG using paint appears to overcome the problem, reducing NG release rates by two orders of magnitude.

It is therefore recommended that timber roofs where positive NG results have been obtained up to 1000 mg/kg should be treated on the inner surface with fire retardant paint, as described in Section 2.2.1. This should significantly reduce the NG emissions from the roof. Only a proportion of NG emitted on the upper untreated surface would be expected to enter the building, depending on the nature of the outer roof covering and size of gaps between boards. Where levels over 1000 mg/kg are detected, it is recommended that both sides of the roof be treated with fire retardant where practicable.

Further trials are in progress to determine whether a reduction in effectiveness of the fire retardant paint occurs with time. The results will be reported in a supplement to this document.

Prior to building occupation (and after renovation) the level of NG within air in each building could be checked by air monitoring as a confidence measure.

APPENDIX 1

Proposal for experimental Trials to Evaluate the Hazards of Explosively Contaminated Wooden Roofs

Introduction

Royal Ordnance has compiled and developed information on permissible levels of various explosives in land which can be used in differing situations. This information evaluates the toxicological hazards of these chemicals and sets levels above which the soil is classed as explosive.

The effect and permissible levels of explosives in other matrices such as wooden roofs, however, is not known. It has been determined experimentally that wooden roofs of explosive-processing buildings can be contaminated by nitroglycerine and, presumably, other volatile aliphatic nitrate esters which may have been used in the building.

It is proposed to carry out experimental trials to attempt to find the information needed to define the levels of permissible contamination by this type of explosive.

Proposal

The proposed work falls into three logical phases which would be carried out sequentially as the conclusion of each affects the next.

Phase One

The results of the recent work, carried out on contaminated wooden roofs from buildings on South Site, suggest that a complex mixture of contaminants may be present. Samples found to contain nitroglycerine frequently show several other GC/TEA peaks. As some of these peaks are significant in size they need to be identified as to whether they are other aliphatic nitrate esters.

This first section of this phase would be to obtain the mono- and di-nitroglycerols, wherever possible, and to define their appearance on the GC/TEA traces. Both the dinitroglycerols and one of the monoglycerols [two isomers of each] are available in small quantities from RO Summerfield for £50 each.

This evaluation will require four hours for analysis, but it is recommended that a further four hours are used for preliminary GC/MS work to be performed. The latter would investigate the detection limits for nitroglycerine, the selectivity of GC/MS in SIM mode for analysis of wood sample extracts, and the robustness of this type of analysis.

The second section of this phase would be a preliminary study of the affinity of nitroglycerine to the wood matrix. If it can be shown that nitroglycerine-contaminated wood will not surrender its contamination even under extreme conditions, then there is no toxicological threat.

The proposed experimental work would take place on wooden roof planks found to be heavily contaminated by nitroglycerine. [Building R603 on South Site would be an ideal location].

The first series of experiments would involve raising the temperature of sections of these planks to approximately 50°C. Air surrounding the sample would be extracted and passed through a trapping system which would be analysed for nitroglycerine after an extended period of time. If insignificant amounts of nitroglycerine were found, higher temperatures may be examined.

Each sample would require four hours and it is recommended that at least four samples are used in order to confirm any trend inferred. It is estimated that a further sixteen hours will be required to mobilise and confirm the trial technique. Minor equipment, glassware and trapping systems, will be required to an estimated maximum cost of £500.

The second series of experiments would be to evaluate the effect of water penetration on the nitroglycerine contamination. Sections of contaminated wooden planks would be steeped in water, with gentle agitation, for several days. The surrounding water would then be analysed for significant levels of nitroglycerine.

It is recommended that at least four samples should be processed and this will require approximately eight hours analytical time.

A short form report would be produced at the end of phase one and it is estimated that this would take an additional eight hours. From these investigations in phase one, evidence may suggest that only very high nitroglycerine levels in wooden roofs need to be remediated. If, however, nitroglycerine does leave the contaminated wood relatively easily, then phase two trials are suggested.

Phase Two

An investigation into the feasibility of neutralisation or encapsulation by varnish etc. of the contaminating nitroglycerine in situ. Samples required would be similar to those used in phase one. A sample would be sprayed with one of the following; acetic acid in acetone, nitric acid in acetone, ammonia in acetone, or epoxi resin amine hardener dissolved in acetone. [It is suggested that a minimum of four samples are used for each treatment]. The samples would then be stood to mature, initially for one week, and then analysed for nitroglycerine and compared to a control. It is estimated that each batch of four sample would require eight hours analytical time.

To evaluate the effectiveness of encapsulation, it is proposed to varnish at least eight contaminated samples. When thoroughly dry, these samples would then be subjected to the phase one tests of heating and steeping in water. The cost of this trial would be as per phase one costs excluding its mobilising costs.

It would be possible to extend this study to include environmental cycling, however, it is felt that the expected cost

of such work makes it preferable to be performed in phase three.

Phase Three

This provides the opportunity to extend/add to the experimentation according to the results from phases one and two, thus only tentative suggestions can be made. No costings are given and can only be prepared as a result of phases one and two.

Flammability:

If the results of phase one show that significant levels of nitroglycerine do not pose a toxicological threat then the enhancement of flammability may need to be considered. This may also need to be considered if encapsulation is proven to be successful.

Toxicity:

If phase one trials show that wood contaminated by nitroglycerine also shows significant levels of other aliphatic nitrate esters then their toxicity needs to be evaluated.

Environmental Cycling:

If phase two encapsulation trails are successful then environmental cycling of several samples may be appropriate.

APPENDIX 2

ANALYSIS OF ROOFING TIMBERS FOR THE PRESENCE OF NITROGLYCERINE

Written by: Dr. D. G. Malcolm . . . . . .

Approved by: Dr. G. Bulloch . . . . . .

Introduction

Analysis of building materials for the presence of explosive contamination is highly dependent upon suitable and appropriate sampling protocols. It is expected that the highest concentration of contamination would be at, or near, the surface where contamination occurred. In explosive or propellant stoves where materials were dried at elevated temperatures, it would be expected that the more volatile explosives would permeate the atmosphere of the stove, contaminating any absorbing surfaces such as wooden roofs. From a common sense viewpoint, it would be expected that this type of contamination would result in a somewhat homogeneous distribution in the wooden roof.

The requirement for this work was for more than one reason:

- There is a possible re-use of the wooden timbers assuming that contamination is not excessive.
- Certain buildings have historic interest where minimum decontamination damage is desirable.
- Further understanding of the mode of contamination, normal or abnormal distributions, would aid the formulation of correct sample protocols.

Sampling

A known colloidal propellant stove, R603, was chosen for investigation. This choice was governed by several factors;

- the building had a timber roof,
- the building was disused, and
- the building had been the centre of a previous investigation.

This previous investigation was hampered by the available analytical techniques but suggested widely different levels of nitroglycerine contamination. The detection limit for this previous work was in the order of several hundred milligrams per kilogram of sample because of interferences. Re-sampling of the roof followed the previous sampling protocol [see Appendix A] and the samples taken were submitted to ESG Chorley Laboratories for low level nitroglycerine analysis.

Analysis

10g of sample were extracted by 40ml of acetone containing 10g anhydrous magnesium sulphate for an extended period by reciprocal agitation. The extract was filtered down to a pore size of 0.45 μm, into autosampler vials. These were then pre-screened for high nitroglycerine levels by HPLC. Those sample extracts which did not contain substantial levels of nitroglycerine [«500mg/kg] were then analyzed by GC-TEA to an approximate detection limit of 1mg/kg. It is to be noted that the soil residential detection limits are approximately 0.1mg/kg which is ten-fold lower than for wood extracts. This difference is due to the very significant organic co-extractants obtained from wood samples. Further, HPLC detection limits for wood extracts are damaged, allowing for detection of nitroglycerine only down to 100-200mg/kg of sample.

Results

Appendix B tabulates the results from the twenty samples. Those samples marked with one asterisk were only analyzed by HPLC due to the excessive nitroglycerine levels. Samples marked with two asterisks were analyzed by both techniques but GC-TEA analysis exceeded the detector range [»40mg/kg], hence tentative HPLC results are reported. It is also to be noted that, to the detection limit of 1mg/kg of sample, EGDN, Tetryl and TNT were not present in any of the samples. In most sample analyses, however, analysis

by GC-TEA provided several unknown, relatively large peaks. In some cases these unknown peaks would exceed the height of the nitroglycerine peak found in the extracts.

Discussion

The results obtained from the current set of samples confirms the previous conclusions formed for the roof of R603. These conclusions are rather unexpected in that the nitroglycerine levels vary greatly in different samples. It was expected that vapour phase transportation of nitroglycerine would result in a somewhat more even level of contamination.

All samples analyzed did show nitroglycerine contamination although the highest level found was approximately 13,000mg/kg and the lowest approximately 1mg/kg. If this type of variation is typical, then a high of 1000mg/kg could result in a low of 0.1mg/kg. In the latter case, the low would be well below the detection limits and so would be classed as uncontaminated. This will have serious implications to any interpretation of contamination based upon limited sampling of roofing timbers.

The unknown peaks observed in a number of GC-TEA chromatograms had retention times longer than EGDN but shorter than nitroglycerine. It would be expected that the compounds have boiling points between that of EGDN and nitroglycerine because of the non-polar column phase. The specific detection system of the TEA would also suggest that these compounds are nitrogen-containing materials. It is highly likely that these compounds are degradation products of nitroglycerine, such as dinitroglycerol [two isomers] and mononitroglycerol [two isomers]. Confirmation of the relative retention times for these materials will be documented if these compounds can be obtained. It would be expected that these compounds would be less energetic and less sensitive than nitroglycerine, but their relative toxicities cannot be surmised.

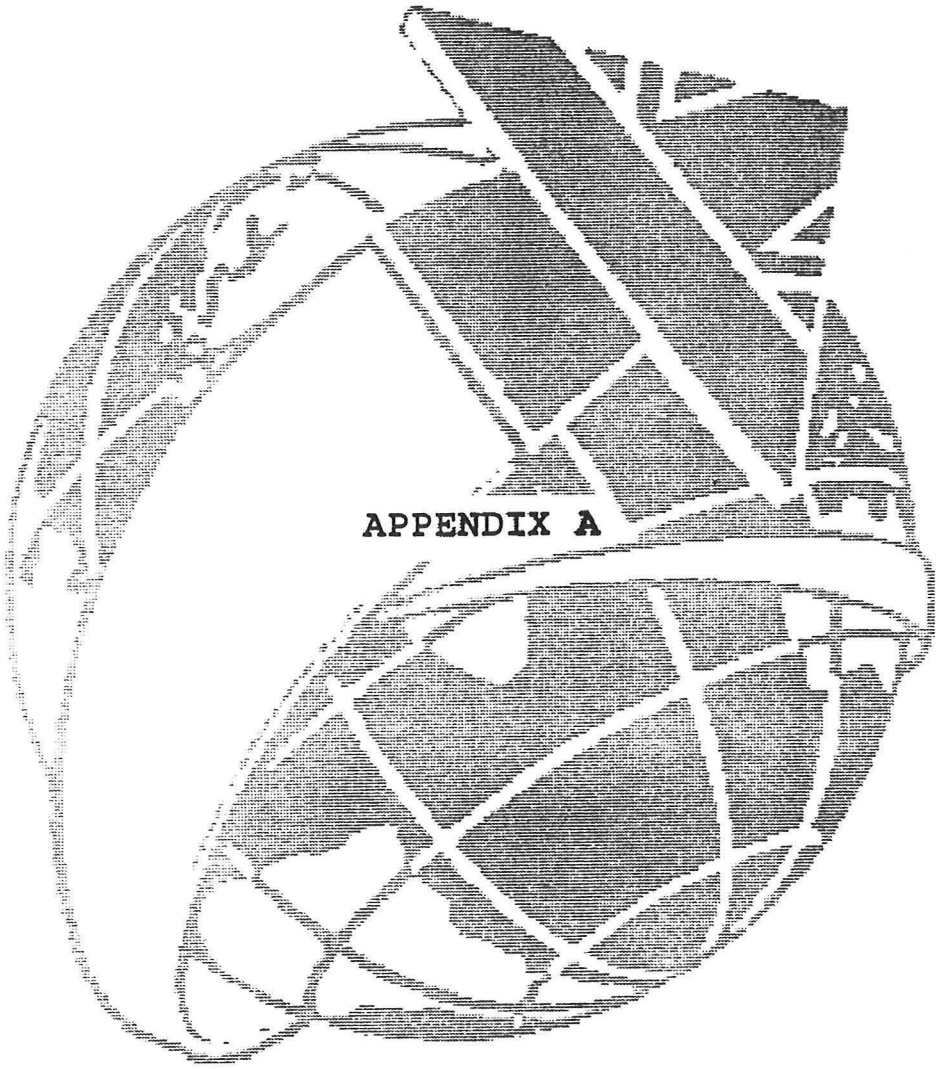
Conclusions

Contamination of wood roofs by airborne deposition of nitroglycerine vapours results in widely varying levels of contamination across the roof.

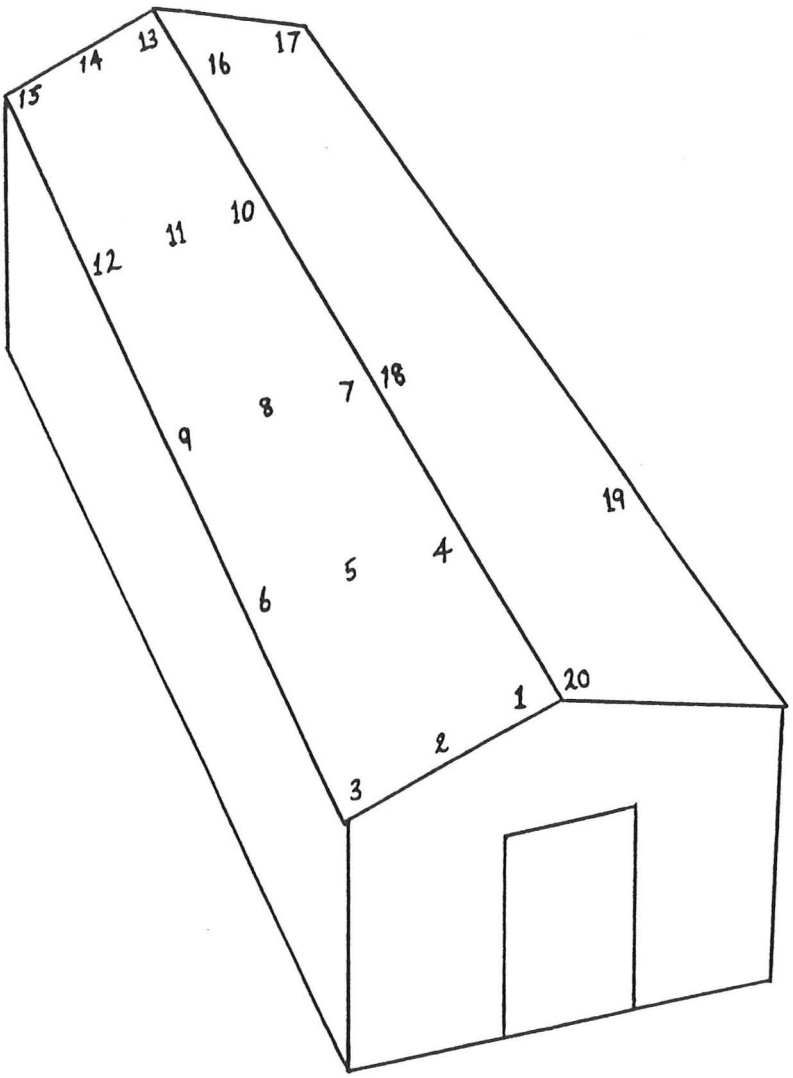
Great care should be taken when devising sampling protocols to investigate such contamination in order to avoid gross underestimation or overestimation.

It is difficult to envisage that the re-use of this type of wood could be profitable because the explosive analysis of such samples is excessively expensive.

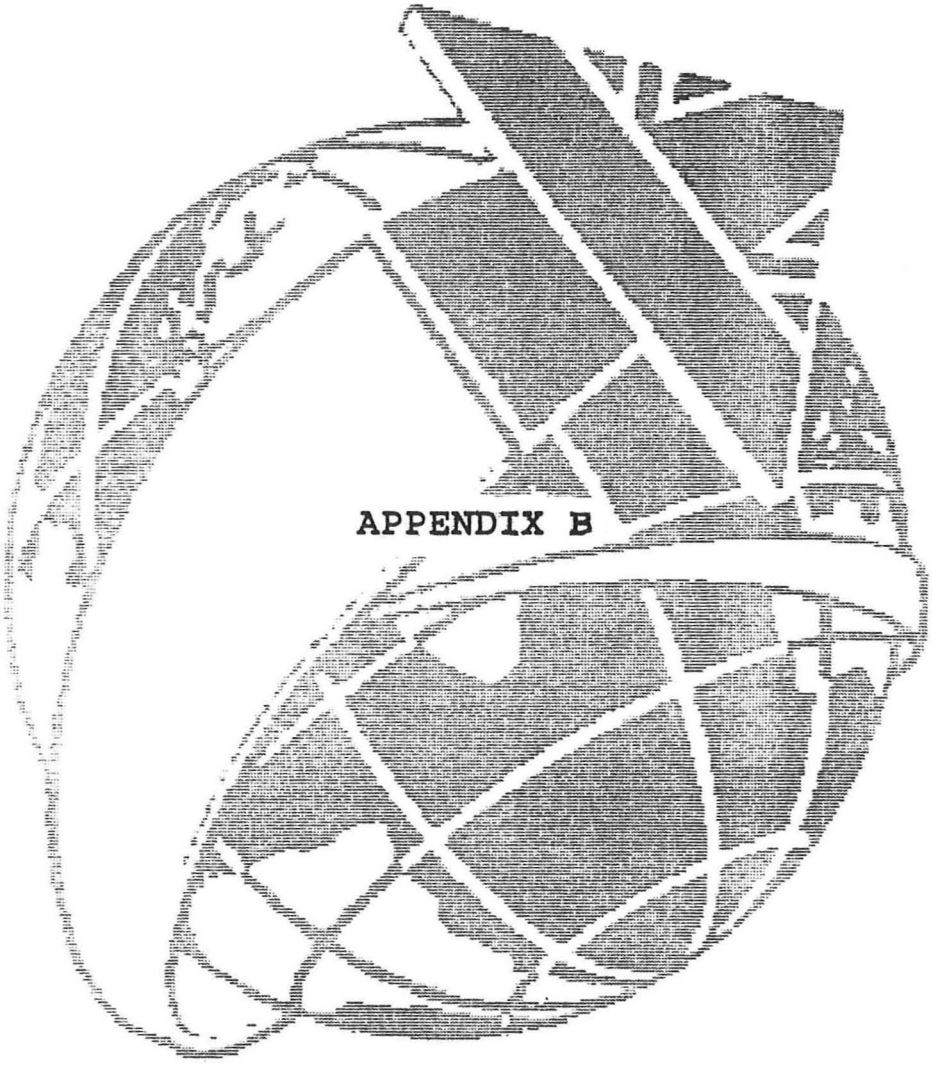
It appears that the wood matrices may not only contaminated by nitroglycerine, but may also have significant levels of mononitro- and dinitro-glycerols.



APPENDIX A



Sampling of R603



APPENDIX B

Sample Number	Laboratory Number	Techniques used	NG [mg/kg]
WASS 1	LNC/512/R/94		27.9
WASS 2	LNC/513/R/94	* *	40
WASS 3	LNC/514/R/94		740
WASS 4	LNC/515/R/94		1.8
WASS 5	LNC/516/R/94		16.6
WASS 6	LNC/517/R/94		2.2
WASS 7	LNC/518/R/94		3.8
WASS 8	LNC/519/R/94		10.5
WASS 9	LNC/520/R/94		1.3
WASS 10	LNC/521/R/94		35
WASS 11	LNC/522/R/94		16.9
WASS 12	LNC/523/R/94		15.9
WASS 13	LNC/524/R/94	*	1915
WASS 14	LNC/525/R/94	*	13245
WASS 15	LNC/526/R/94	*	1320
WASS 16	LNC/527/R/94	*	4575
WASS 17	LNC/528/R/94	*	625
WASS 18	LNC/529/R/94		3.1
WASS 19	LNC/530/R/94		4.1
WASS 20	LNC/531/R/94	*	1510

Key: [Techniques used]

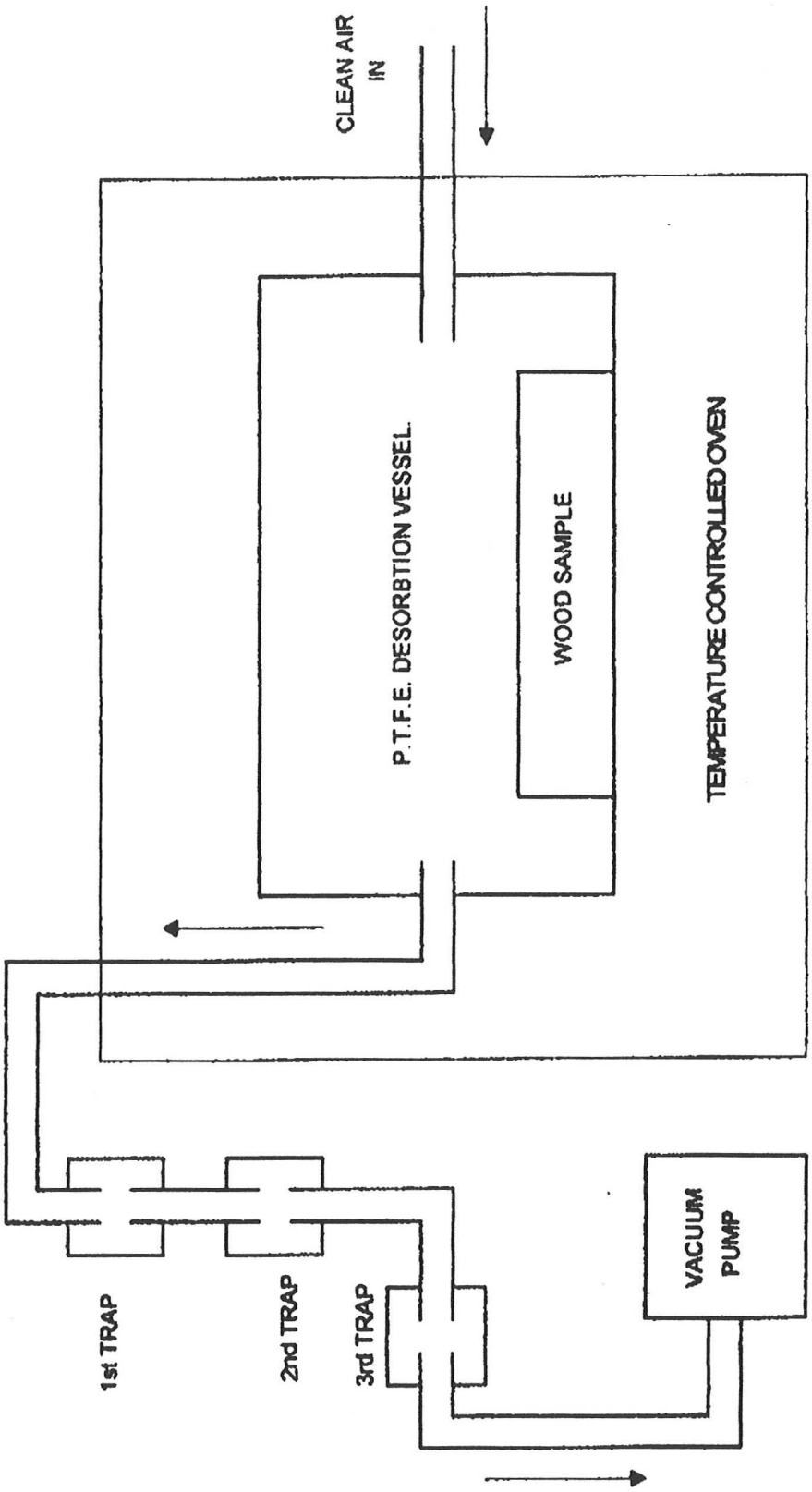
HPLC and GC/TEA

* HPLC only

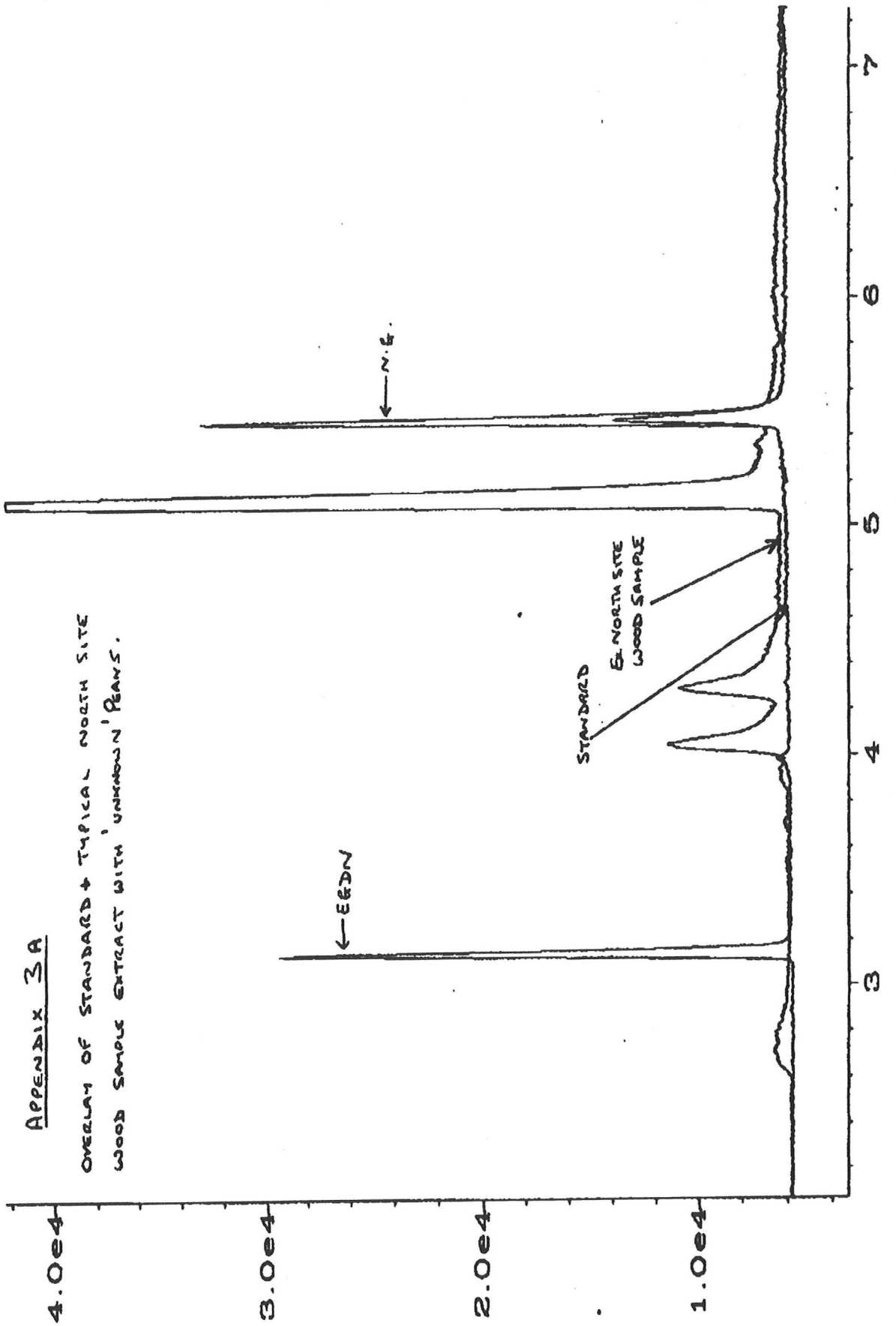
* * HPLC and GC/TEA but HPLC result used

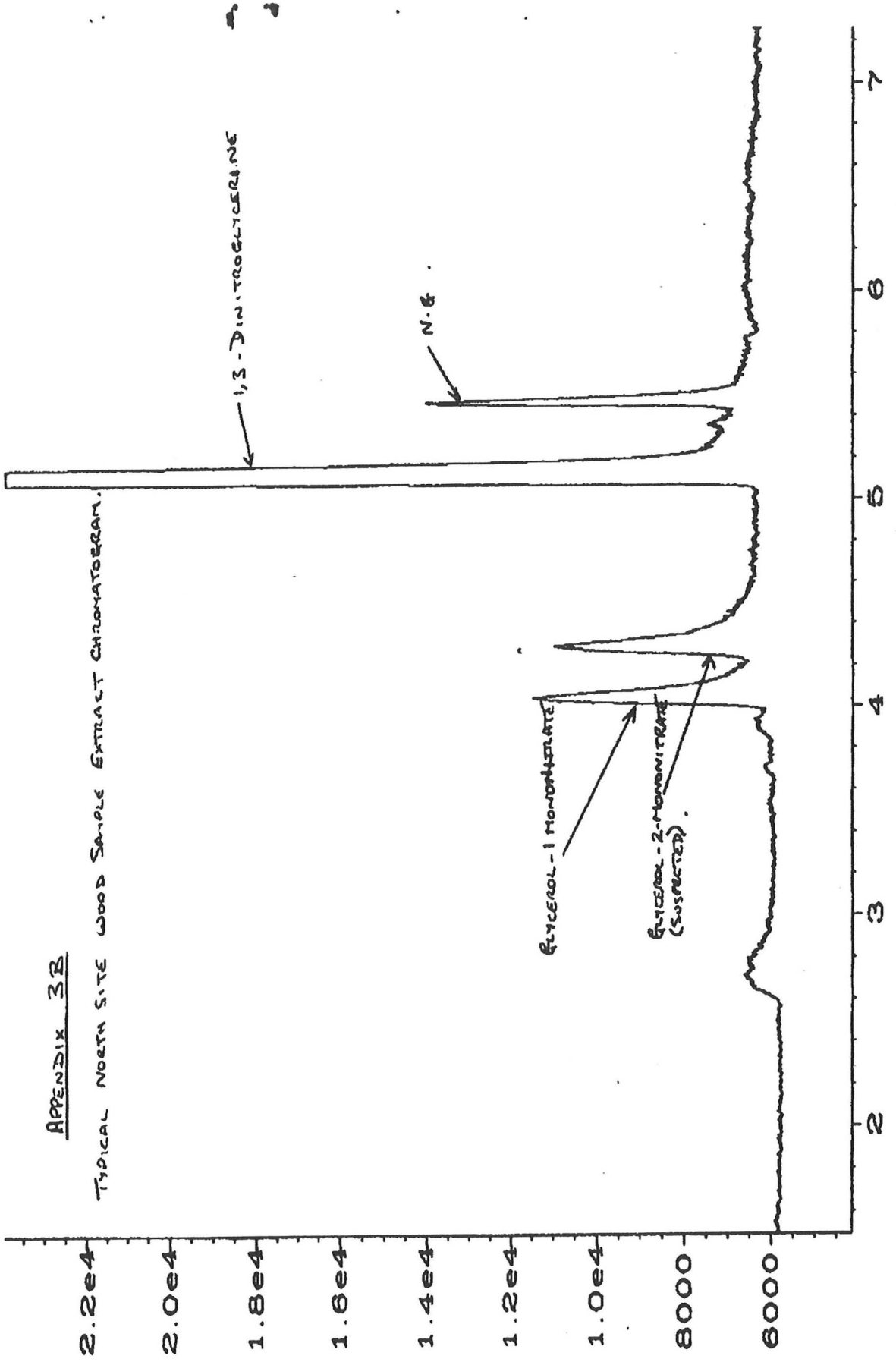
APPENDIX 3

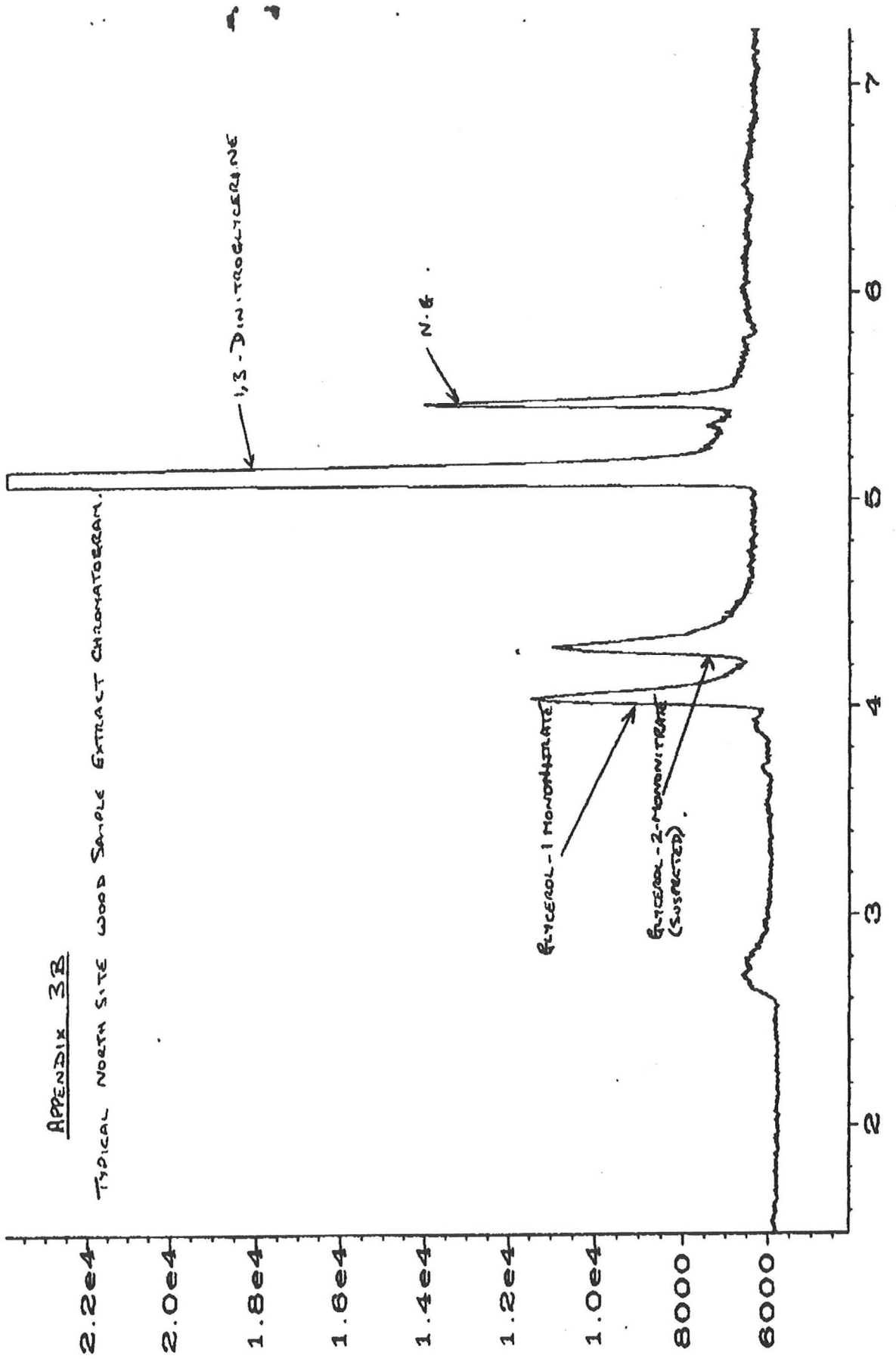
APPENDIX 2


CLEAN AIR IN
P.T.F.E. DESORBTION VESSEL
WOOD SAMPLE
TEMPERATURE CONTROLLED OVEN
1st TRAP
2nd TRAP
3rd TRAP
VACUUM PUMP

APPENDIX 4


APPENDIX 3A
OVERLAY OF STANDARD + TYPICAL NORTH SITE WOOD SAMPLE EXTRACT WITH 'UNKNOWN' PEAKS.
EEDN
STANDARD
E. NORTH SITE WOOD SAMPLE
N.E.
4.0e4
3.0e4
2.0e4
1.0e4
3
4
5
6
7


APPENDIX 3B
TYPICAL NORTH SITE WOOD SAMPLE EXTRACT CHROMATOGRAM.
1,3-DINITROGLYCERINE
N.G.
GLYCEROL-1 MONONITRATE
GLYCEROL-2-MONONITRATE (SUSPECTED)
2.2e4
2.0e4
1.8e4
1.6e4
1.4e4
1.2e4
1.0e4
8000
6000
2
3
4
5
6
7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TYPICAL NORTH SITE WOOD SAMPLE EXTRACT CHROMATOGRAM.
1,3-DINITROGLYCERINE
N.G.
GLYCEROL-1 MONONITRATE
GLYCEROL-2-MONONITRATE (SUSPECTED).
2.2e4
2.0e4
1.8e4
1.6e4
1.4e4
1.2e4
1.0e4
8000
6000
2
3
4
5
6
7

APPENDIX 5

6 Ordering Information

To order Porapak Rdx cartridges and accessories, contact your Waters representative.

Table 2 Porapak Rdx Cartridges and Accessories

Item	Part Number
Porapak Rdx Cartridges (Box of 30)	WAT047220
Nova-Pak® C_8 3.9 mm x 150 mm column	WAT035876
Nova-Pak C_8 3.9 mm x 100 mm cartridge column	WAT052805
Nova-Pak CN HP 3.9 mm x 100 mm cartridge column	WAT044245
End Connector Kit (required for cartridge column)	WAT037525
Waters Vacuum Manifold, 12-position	WAT054750
Waters Vacuum Manifold, 16-position	WAT054755
Tubing, Tefzel®, 1/8-inch O.D. x 0.040-inch I.D.	WAT023344
Sep-Pak Vac Adapter	WAT054260
60-mL Sep-Pak Reservoir	WAT024659

Refer to the *Waters Chromatography Handbook* for a complete list of column accessories and supplies.

7 Warranty/Service Information

Waters Chromatography replaces without cost any cartridge that fails to perform satisfactorily, if notified within 90 days from your receipt.

Waters Sep-Pak® Vac
Porapak® Rdx Cartridges
Instruction Sheet

Waters Chromatography
34 Maple Street
Milford, MA 01757
047224TP, Rev 0
April 1994

8 Specifications

Waters manufactures Porapak Rdx cartridges to exacting background specifications in our ISO-9002-certified manufacturing facility. A 100-µL injection of properly prepared laboratory reagent blank (see Sections 2 through 5) contains less than 0.4 ng* of any individual contaminant in the chromatographic region defined by the analytes listed in Table 1. (* of RDX equivalent)

References

M.G. Winslow, B.A. Weichert, R.D. Baker, "Determination of Low-level Explosive Residues in Water by HPLC: Solid-phase Extraction vs. Salting-out Solvent Extraction," *Proceedings of EPA Seventh Annual Waste Treating and Quality Assurance Symposium*, 1991.

T.F. Jenkins, P.H. Miyares, K.F. Myers, E.F. McCormick, A.B. Strong, "Comparison of Cartridge and Membrane Solid-phase Extraction with Salting-out Solvent Extraction for Preconcentration of Nitroaromatic and Nitramine Explosives in Water," *CRREL Special Report 92-25*, 1992.

1 Introduction

Waters Porapak™ Rdx Sep-Pak™ Vac Cartridges are designed for the solid-phase extraction of nitroaromatic and nitramine explosives and their degradation products (Table 1). Use these convenient sampling devices for reproducibly concentrating nitroaromatic and nitramine explosives present in groundwater and surface water at concentrations down to the sub-ppb level. Porapak Rdx Sep-Pak Cartridges meet the sample-preparation requirements of EPA Solid Waste 846 Method 8330.

Porapak Rdx Sep-Pak Vac Cartridges consist of Porapak Rdx resin, a specially prepared divinylbenzene/vinylpyrrolidone copolymer, packed in high-purity polyethylene syringe barrels.

Table 1 Explosives Analytes

Abbreviation	Analyte
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
1,3,5-TNB	1,3,5-Trinitrobenzene
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
1,3-DNB	1,3-Dinitrobenzene
2,4,6-TNT	2,4,6-Trinitrotoluene
Tetryl	Methyl-2,4,6-trinitrophenylnitramine
NB	Nitrobenzene
3,5-DNA	3,5-Dinitroaniline
2,4-DNT	2,4-Dinitrotoluene
3,4-DNT	3,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
2-Am-DNT	2-Amino-4,6-dinitrotoluene
4-Am-DNT	4-Amino-2,6-dinitrotoluene
4-NT	4-Nitrotoluene
2-NT	2-Nitrotoluene
3-NT	3-Nitrotoluene

2 Conditioning the Cartridge

Before loading the sample onto the cartridge, condition the cartridge to activate the Porapak Rdx packing material.

Once you have activated the packing material, do not expose it to air until all of the sample has been loaded. If the cartridge runs dry, repeat the conditioning procedure.

To condition the cartridges:

1. Remove the internal rack from the vacuum manifold.
2. Insert a Sep-Pak adapter into each Porapak Rdx cartridge.
3. Connect the cartridges to the vacuum manifold.
4. Connect Sep-Pak reservoirs to the adapters.
5. Fill each reservoir with 15 mL acetonitrile. Pulse the vacuum pump to start the flow, then let the acetonitrile drip through under gravity alone.
6. Just before each reservoir runs dry, refill the reservoir with 30 mL Milli-Q water.
7. Turn on the vacuum pump and adjust the flow rate with the stopcock valves to draw the water through the cartridge. The flow rate should not exceed 10 mL/min. Close valves.
8. Dispose of the aqueous acetonitrile in the manifold.

3 Loading the Sample onto the Cartridge

To load the sample onto the cartridge:

1. Fill the reservoirs with the water sample that is to be concentrated, or connect sample vessels (see figure).
2. Turn on the vacuum. Use the stopcocks to adjust the flow rate to about 10 mL/min. If you are using the reservoirs, refill them as needed. Empty the vacuum trap as needed.

Make sure the bed does not run dry during loading.

3. After all sample is loaded, apply full vacuum for a few minutes to remove residual water.
4. Turn off the vacuum and open the bleed valve.

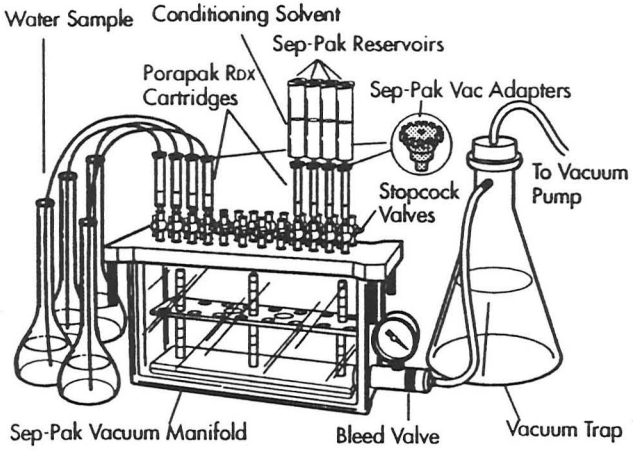
4 Eluting the Sample for Analysis

Before eluting the sample, set up the vacuum manifold with clean collection vessels and needles. To elute the sample:

1. Remove the adapter and reservoir from the cartridge.
2. Put 5 mL acetonitrile into the cartridge. Pulse the vacuum pump to start the flow, then let the acetonitrile drip through under gravity alone. The flow rate should be about 1 mL/min.
3. After acetonitrile stops dripping, turn on the vacuum briefly to draw the remaining acetonitrile through the cartridge.

Be careful when applying vacuum. Too much vacuum may cause the sample to splatter.

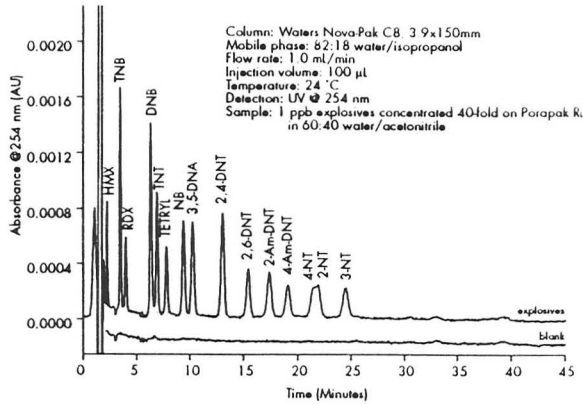
4. Open the manifold and remove the collection vessels.
5. Fill the collection vessels to the 5-mL mark with acetonitrile and vortex to mix thoroughly.
6. Dilute to 40% acetonitrile with reagent-grade water and mix thoroughly The sample is ready for HPLC analysis.



Two Ways to Connect Sep-Pak Vac Cartridges to the Waters Vacuum Manifold

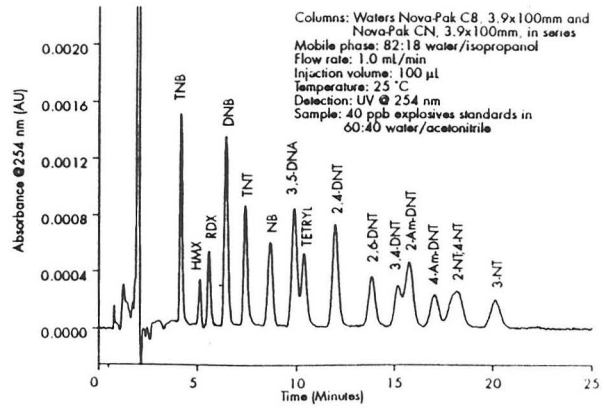
5 HPLC Analysis

Use the single-column separation conditions shown below for most analyses. The chromatogram below compares a standard solution of explosives analytes and a cartridge blank.



HPLC Separation of Explosives Analytes vs Cartridge Blank

Use the alternate 2-column separation conditions shown below for peak confirmation, or to improve quantitation of HMX when interfering substances that elute in the void volume are present. Note the change in elution order.



Alternate Separation of Explosives Analytes