

## **Explosive recovery from hair**

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**Abstract**

Hair is a good solid-phase extraction medium because it picks up substrates both by environmental exposure and by ingestion. Sampling hair has proved to be a useful non-invasive method for detecting illicit drugs. The Society for Forensic Toxicology (SOFT) has accepted drug analysis of hair as a confirmatory technique, and the Substance Abuse and Mental Health Administration SAMHA has reviewed various factors pertinent to use of this technique as legal evidence.<sup>1,2</sup> For these reasons we wished to determine the feasibility of detecting explosives in hair.

This study demonstrated the viability of hair as a surface from which explosive traces can be recovered, showing that as little as one-hour exposure can result in traces of explosives. Contamination of the hair may come by direct contact of the subjects' hair with explosive particles or by secondary contact as the subject hands transfer particles to his/her hair. Furthermore, we have shown that hair can concentrate explosive from the ambient vapor of a variety of military explosives.

The amount of TNT picked up by the hair increases with time and had not reached saturation after 24 hours. The data also suggested that unwashed hair may pick up more TNT than washed hair. The relative vapor pressure of 2,4-DNT is over 4000 times that of TNT; however the sorption of DNT to hair is only about 40 times larger than TNT. In each case, we noted that after 24 hours of exposure saturation of the hair was not achieved.

Keywords: Hair, Explosives, Recovery, Trace

## Introduction

Sampling hair has proved to be a non-invasive method for detecting illicit drugs. Detection of drugs in hair has been accepted as a confirmatory technique by the Society for Forensic Toxicology (SOFT), and the Substance Abuse and Mental Health Administration (SAMHA) has reviewed various factors pertinent to use of this technique as legal evidence.<sup>1,2</sup> Hair is a good solid-phase extraction medium because it picks up substrates both by environmental exposure and by ingestion. Hair synthesis is one of the fastest cellular functions known.<sup>3</sup> As a result, heroin, which is rapidly metabolized in the body, can be found un-metabolized in the hair root bulb (Kalasinsky, K. private communication.). For these reasons it was desirable to determine the feasibility of detecting explosives in hair. Initially only surface contamination was studied.

In the 1980's unpublished work carried out at the Royal Armament Research and Development Establishment (RARDE) by Wardleworth and Ancient found that nitrobenzene (NB) and ethylene glycol dinitrate (EGDN) vapors would absorb to bulk hair. However, these compounds have a very high vapor pressure compared to many common military explosives (Table 1). Milburn continued this work, also unpublished, studying the effects of humidity on sorption of NB and EGDN onto hair. In this study the environmental contamination of hair by the explosives: RDX, TNT, and dinitrotoluene (DNT) were examined. The hair of individuals was tested before and after they handled explosives, and bulk hair samples were examined for which the only exposure mode was the ambient explosive vapour.

## **Methods and materials**

### **Sampling Hair of Explosive Workers**

Four individuals involved in the preparation of dog training kits in an explosive processing area were used as test subjects because their task entail the handling of bulk quantities of C4 (RDX), Semtex (RDX, PETN), PE4 (RDX), TNT, Aquaspex (NG based), and cordtex (PETN).<sup>12</sup> By chance all the subjects were female, most with hair above their shoulders. Initial samples of their hair were taken first thing Monday morning before they had handled any explosives or entered the explosive processing areas. After the subjects washed their hands and donned clean disposable gloves, their hair was swabbed with new ethyl-acetate-washed combs through which clean cotton swabs were threaded. The swabs (2) on the comb were wetted with a 50:50 ethanol/water solution applied using a plastic pipette and excess solvent removed by shaking the comb vigorously. The subjects combed their own hair before sealing the comb in a clean nylon bag. At the time of sampling a control was taken by wetting a comb with the solvent and placing it directly in a clean nylon bag. Subjects 1 and 2 worked in the explosive processing area approximately 4 hours, while subjects 3 and 4 were exposed approximately 7 hours. When the subjects finished work their hair was re-swabbed, as described above, and a control was again taken.

### **Extraction of swabs**

Processing and analysis of swabs was carried out in an explosives controlled environment. The combs were removed from the sealed nylon bag one at a time and the swab removed from the comb using plastic disposable tweezers. Swabs were placed in a soda glass vial and extracted with two 5mL portions of 50:50 ethanol:water while they were pummelled using a glass pipette. The extracted solvent was passed through a tube containing Chromosorb 104 stationary phase on which explosives are retained. The explosives were eluted from the Chromosorb column using

ethyl acetate. The resulting 800 $\mu$ L sample was reduced under nitrogen to approximately 100 $\mu$ L and analysed by Gas Chromatography/Thermal energy analyser (GC/TEA).

A semi-quantitative result was accomplished. The GC ovens were Carlo Erba 8000 series. The injection port was the manufacturer's standard split/splitless type with the narrower of the two liner types offered fitted as standard. The injection port liners were lightly plugged at about their mid-point, over a distance of approximately 10mm, with deactivated silica wool. Samples were injected using SGE (SGE UK Ltd., Milton Keynes, England) type 1BR-7 1 $\mu$ l plunger-in-needle syringes with needle lengths of 70mm. The carrier gas was high purity helium. Three types of GC column were used within the GC oven during analysis, under conditions given in Table 2.

The injection port temperatures were 175°C and had glass liners lightly plugged with deactivated silica wool.

The detectors were Thermedics TEA Model 610 detectors modified as described in reference 4. These instruments as supplied consist of a pyrolysis oven (mounted directly on the side of the gas chromatograph oven), cold trap (not used), ozoniser, chemiluminescence reaction chamber with attached photomultiplier, and photomultiplier signal amplifier.

Samples indicating the presence of explosive on one system would be confirmed by analysis on the remaining two systems. Dilutions were carried out if peaks of suspected explosives were considerably larger than that of the standard. A system blank was ran in between positive samples instead of following positive samples with a standard as described in FEL methods. A maximum of three samples and three blanks were analysed between standards. The results are quantified by comparison of peak area of the sample with that of a standard and are calculated by the following equations.

$$\text{Mass Sample Injected} = \text{Mass Standard Injected} \times \frac{\text{Peak Area}_{\text{sample}}}{\text{Peak Area}_{\text{standard}}}$$

$$\text{Total Mass} = \text{Mass Injected} \times \frac{\text{Total Volume of Sample}}{\text{Volume Injected}}$$

### **Vapour sorption by Bulk Hair**

TNT and RDX were obtained from military sources. Dinitrotoluenes (DNT) were purchased from Aldrich; they ranged in purity from 99% (2,3-DNT, 3,4-DNT) to 98% (2,6-DNT) to 97% (2,4-DNT). Hair was obtained from hair salon sweepings; it was generally black in colour. Experiments were performed with both washed and unwashed hair. The wash procedure consisted of rinsing the hair with a 4.5% sodium lauryl sulphate solution followed by distilled water and air-drying the hair for 48 to 60 hours. (Hair samples were often used while still slightly damp.). Quantities of each explosive were placed in 400mL wide-mouth jars. Weighed amounts of hair (~0.3g), physically separated from the explosive, were closed in the jars. In the case of TNT and 2,4-DNT, the explosive lay freely in the bottom of the jar while the hair was suspended on a watch glass above it. For RDX studies, the hair was weighed into a weighing boat and placed in the bottom of the jar next to a vial containing the explosive. After 1, 3 and 24 hours, samples of hair (~0.1g) were removed, weighed and allowed to stand in 5 mL of acetonitrile overnight. (A blank was also prepared by placing hair in an empty jar and treating as above.) The above experiments were performed in duplicate.

### **GC/ECD analysis**

Analysis of the acetonitrile explosive extract was accomplished using a

Hewlett Packard 5890 gas chromatograph equipped with electron capture detector (GC/ECD) and a J&W Scientific megabore DB-5MS (0.53mm I.D., 7.5 metres, 1.5 $\mu$ m film) column. A summary of GC conditions used is shown in Table 3. Calibration standards for each of the explosives were prepared, and these were analysed prior to the samples and a standard curve was plotted. The explosive detected in the samples was then quantified using the standard curve. The standard curves used a minimum of three points.

## **Results and Discussion**

### **Sampling Hair of Explosive Workers**

The explosives detected are shown in Table 4 both before and after handling. The quantities detected using each of the analytical columns are shown. NG from aquaspex was not detected, this may be due to the fact that this particular explosive is sealed sufficiently to prevent contamination. It is possible that the NG does not stick the surface of the hair to the same extent as the less volatile explosives and therefore may have a lower persistence. It is interesting to note that the highest exposure time does not necessarily mean the highest quantity detected. This would suggest that the main mechanism of the contamination may be contributed to physical contact and transfer of the explosive.

Subject 1 had hair slightly shorter than shoulder length and the style was such that it sometimes got in their eyes. The unconscious act of brushing her hair out of her eyes may have contributed significantly to the comparatively large quantities of explosives recovered. Subject 2 had curly shoulder length hair which was relatively clear of the eyes, subject 3 had the shortest hair and this may account for comparatively small amounts of explosive recovered. Subject 4 had wavy slightly shorter than shoulder length hair. Interestingly no RDX was detected on subject four even though all four subjects handled all the explosives above, albeit to different extents. If RDX was transferred to the hair primarily by contact between the hands and hair, it is possible Subject 4 did not touch her hair after handling the RDX-containing explosives.



## Sorption by Bulk Hair

GC/ECD analysis of the unexposed hair acetonitrile extract gave rise to many peaks on the chromatogram. Figure 1 shows a typical “blank,” an acetonitrile extraction of unexposed hair. Figure 2 shows a typical chromatogram of hair exposed to TNT. Figure 3 shows the amount of TNT recovered from the hair as a function of time. Duplicate studies exhibited a rather broad range; nevertheless the results make it clear that in as little as one hour TNT had been sorbed by the hair. The quantity of TNT picked up by the hair increases with time and had not reached saturation after 24 hours. It should be emphasized that the methodology of these studies was such that explosives could only be transferred to the hair through the vapor phase. The data also suggested that unwashed hair may pick up more TNT than washed hair. This trend is more obvious with 2,4-DNT. This is in line with the unpublished observations of Wardleworth and Ancient. It may indicate a correlation between the volatility of the explosive and its sorption to washed versus unwashed hair, or it may be an artifact of the dampness of the washed hair. Damp hair may swell allowing the more volatile explosive to penetrate deeper into the follicle, thereby making it more difficult to remove. Another reason maybe that the water, due to its polar nature occupied the majority of adsorption sites.

Hair exposed to 2,4-dinitrotoluene exhibited four closely separated peaks in an area of the chromatogram vacant in the blank hair specimens (retention time 6.8 to 8.0 minutes) and is shown in Figure 5.

It was suspected other DNT isomers, that may be present as contaminants of 2,4-DNT, were also absorbed by the hair. Comparison of the chromatogram of authentic samples of 2,3- 2,6, and 3,4-DNT confirmed this conclusion. DNT having a much higher vapor pressure than TNT is sorbed to a much higher extent than TNT. Interestingly, the relative vapor pressure of 2,4-DNT is over 4000 times that of TNT; however the sorption of DNT to hair is only about 40 times

larger than TNT. In each case, we note that after 24 hours of exposure saturation of the hair was not achieved.

## Conclusions

The study has demonstrated the viability of hair as a surface from which explosive traces can be recovered, showing that as little as one-hour exposure can result in detectable traces of explosives being recovered. Contamination of hair may arise by direct contact of the subjects' hair with an explosive or by secondary contact as the subject hands transfer particles to his/her hair. Furthermore, it has been shown that hair can concentrate explosive from the ambient vapor of some military explosives.

There are a number of areas for future research on this topic. Persistence of the explosive on the hair over time and after shampooing must be determined before the usefulness of the technique can be properly assessed. The pigmentation and medullation of the hair and the sex and race of the individual have been shown to have an effect on degree of drug sorption and metabolic incorporation. The impact of these factors on sorption of explosive must be determined. The results of this and similar studies on drug binding may elucidate binding modes of the substrate to hair. Thus, far this study has addressed only the environmental contamination of hair with explosives. Involuntary ingestion of explosives via inhalation or sorption through skin may also be detectable. Possible metabolites need to be identified.

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10. These are common abbreviations for the following: TNT 2,4,6-trinitrotoluene;; PETN pentaerythritol tetranitrate; TATP triacetone triperoxide; HMX octahydro-1,3,5,7,-tetranitro-1,3,4,5-tetrazocine; RDX hexahydro-1,3,5-trinitro-s-triazine; NG nitroglycerin; EGDN ethyleneglycol dinitrate; DNT dinitrotoluene; DSC differential scanning calorimetry.

Explosive	MW g	m.p. °C	T <sub>exp</sub> °C	Vapor pressure (torr or mm Hg)				Water-solubility			
				@20C	Ref	@100C	Ref	g/100 g @ 20°C	Ref		
EGDN	152	Liquid	237	0.038	7	17	6, calc	0.68	20°C	7	
NG	227	13	270	0.00025, 0.0015	6,7	0.41	6, calc	0.18	20°C	7	
TATP	222	94	227*	Sublimes	Observation						
2,4-DNT	182	69	270	0.019	8			0.254		7	
TNT	227	81	288	4.5E-06	5, calc	0.040, 0.11	5,7	0.013	20°C	5,7	
PETN	316	141	210	1 to 6 E-08	5 & 9 calc	9.0E-04	5, calc	0.0002	20°C		
RDX	222	204d	217	1 - 3 E-09	5 & 9 calc	9.1E-05	5, calc	0.005	20°C	5	

\* DSC exothermic maximum at 20°/min.

*Table 1. Vapour pressures and solubilities of some explosives*

Column	Oven Program	Carrier pressure
SGE type 12QC2/BP1 12 metre polyimide clad silica, 0.22mm i.d., 0.33mm o.d., coated with bonded dimethylsiloxane 0.25µm film thickness.	75°C/1min + 20°C/min to 200°C/2 min	250 kPa
SGE type 12QC2/BP5 12 metre polyimide clad silica, 0.22mm i.d., 0.33mm o.d., coated with bonded 5% diphenyl-dimethylsiloxane 0.25µm film thickness.	75°C/1min + 20°C/min to 200°C/2 min	250 kPa
Chrompack CP-Sil-19CB, 4 metres cut from 25 metre polyimide clad silica, 0.25mm i.d., 0.39mm o.d., coated with bonded 7% cyanopropyl-7%phenyl- 1% vinyl- dimethylsiloxane 0.21µm film thickness.	65°C/1min + 20°C/min to 250°C/2 min	70 kPa

*Table 2. Summary of GC conditions*

Explosive to be detected	Oven Program
TNT, 2,4-DNT	60°C/30secs +15°C/min to 250°C/1 min. The injector temperature was 250°C and the detector temperature, 300°C.
RDX	65°C/2min +20°C/min to 280°C/1min. The injector temperature was 175°C and detector temperature, 300°C.

*Table 3. Summary of conditions used for GC/ECD analysis*

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**Initial Explosive (ng)**

**Final Explosive (ng)**

Subject no.	Sex	Length Hair (cm)	Color Hair	TNT	PETN	RDX	Hours exposed	TNT (CPSIL)	TNT (BP1)	TNT (BP5)	TNT average	PETN (CPSIL)	PETN (BP1)	PETN (BP5)	PETN average	RDX (CPSIL)	RDX (BP1)	RDX (BP5)	RDX average
1	F	Medium ~15cm, straight	grey /black	0	0	13	4	8504	9769	6050	<b>8108</b>	258	187	285	<b>243</b>	2160	1630	2162	<b>2840</b>
2	F	Medium ~15cm, curly	red	0	0	0	4	154	182	82	<b>139</b>	66	85	64	<b>72</b>	936	941	738	<b>872</b>
3	F	Short ~7.5cm, straight	grey/ black	0	0	0	7	28	26	19	<b>24</b>	144	298	237	<b>226</b>	21	24	12	<b>19</b>
4	F	Short ~9cm, wavy	grey	0	0	0	7	222	225	225	<b>224</b>	111	95	159	<b>122</b>	-	-	-	-

*Table 4. Hair of Explosive Workers Before and After Work with Explosives*



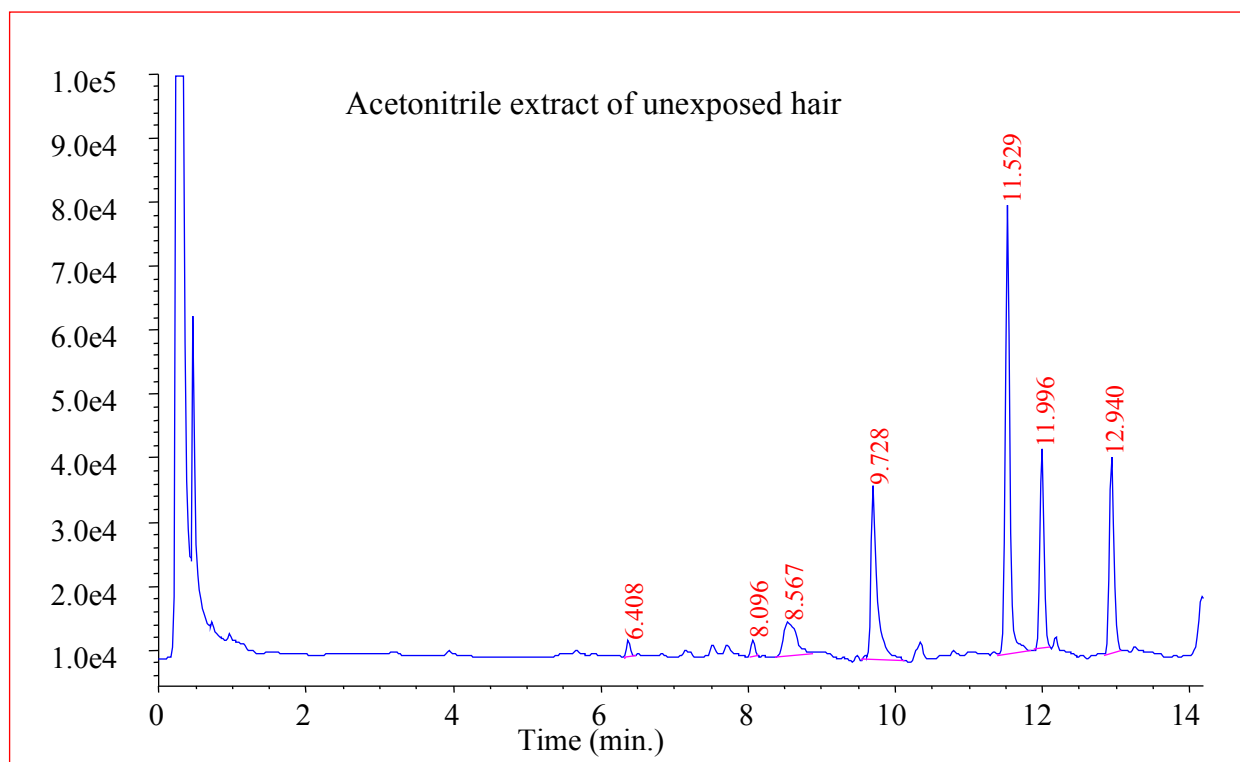


Figure 1. Chromatogram of acetonitrile extract of unexposed hair

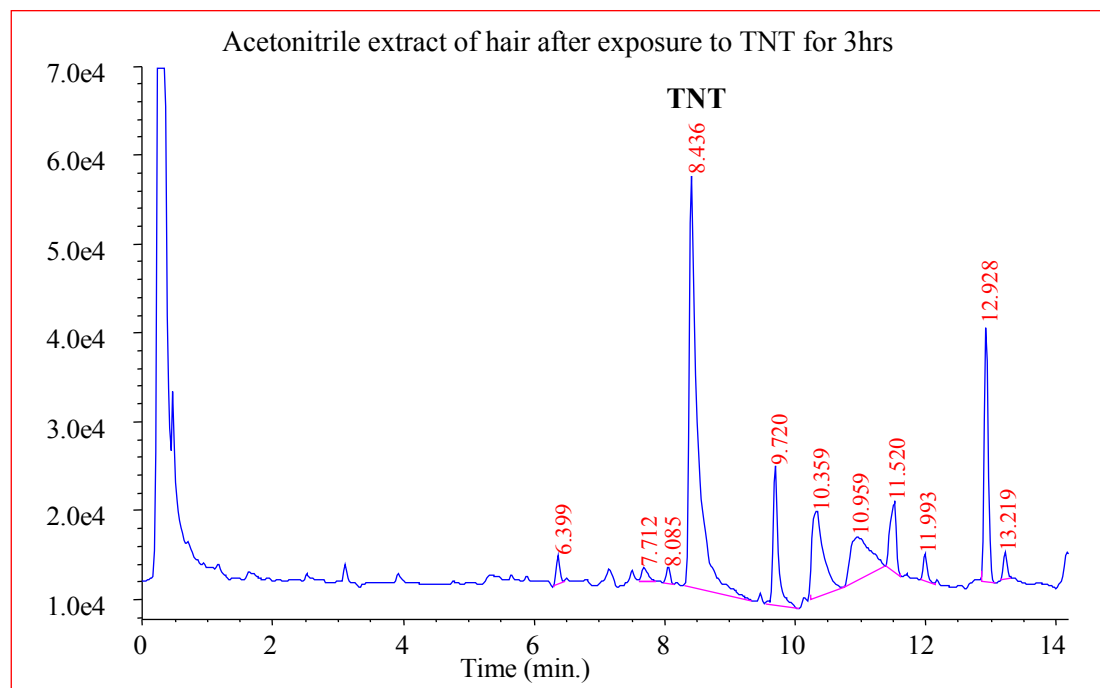


Figure 2. Chromatogram of acetonitrile extract of hair after 3hrs exposure to TNT

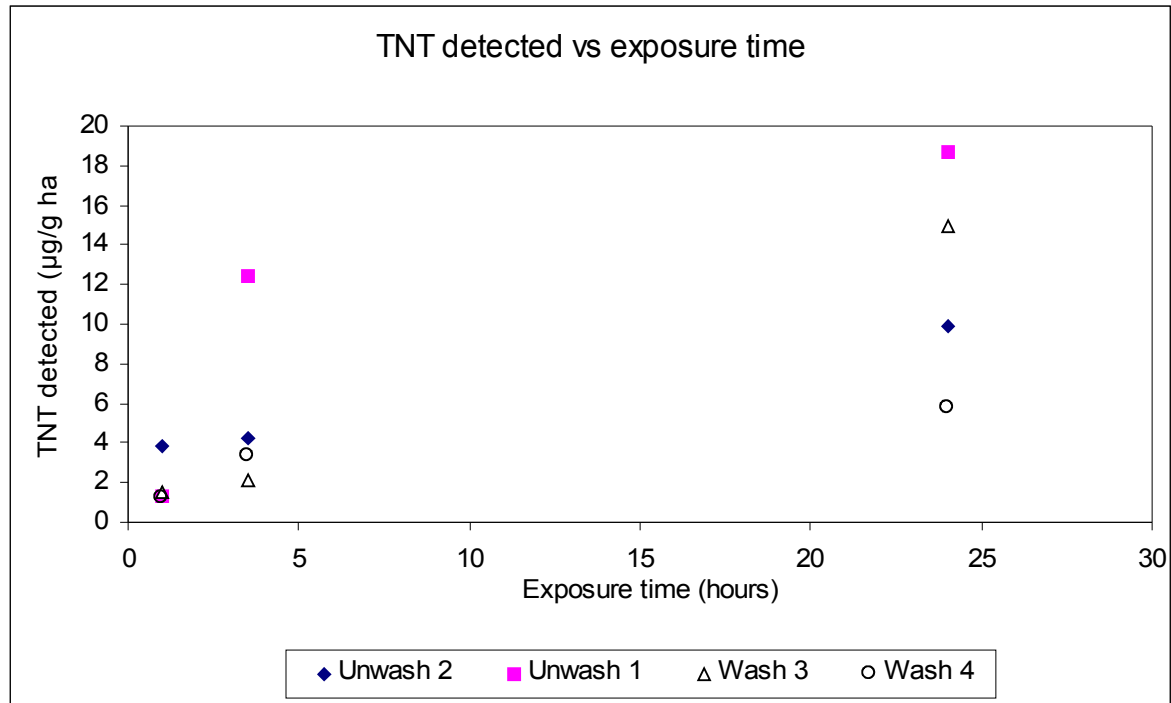


Figure 3. TNT detected from washed and unwashed hair vs exposure time

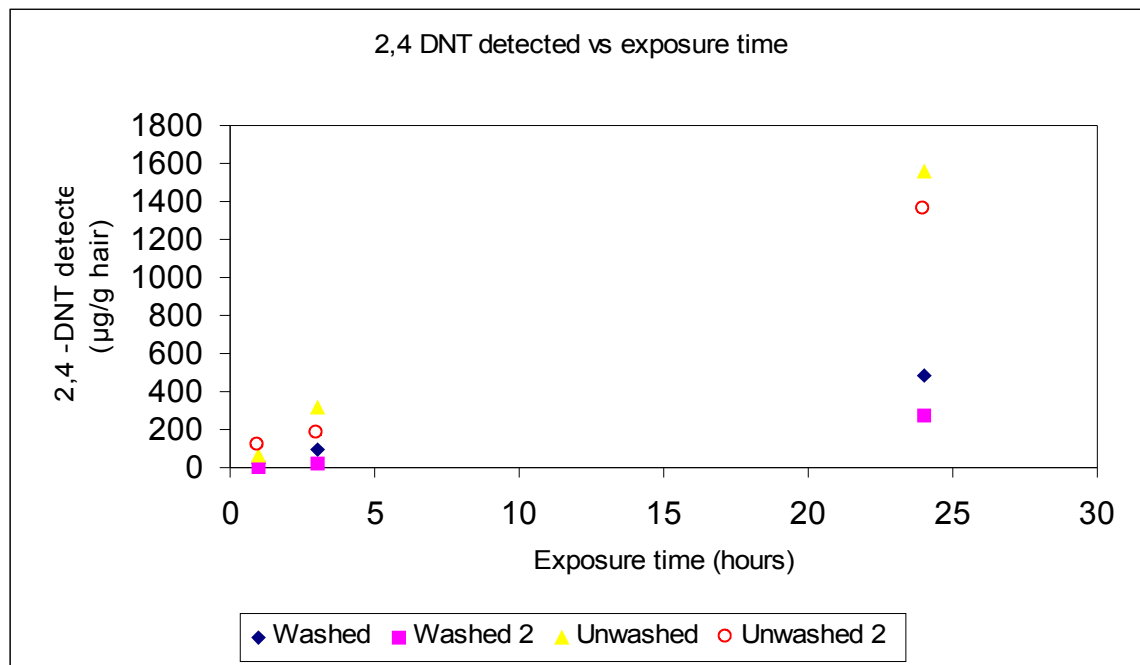


Figure 4. 2,4- DNT detected from washed and unwashed hair vs exposure time

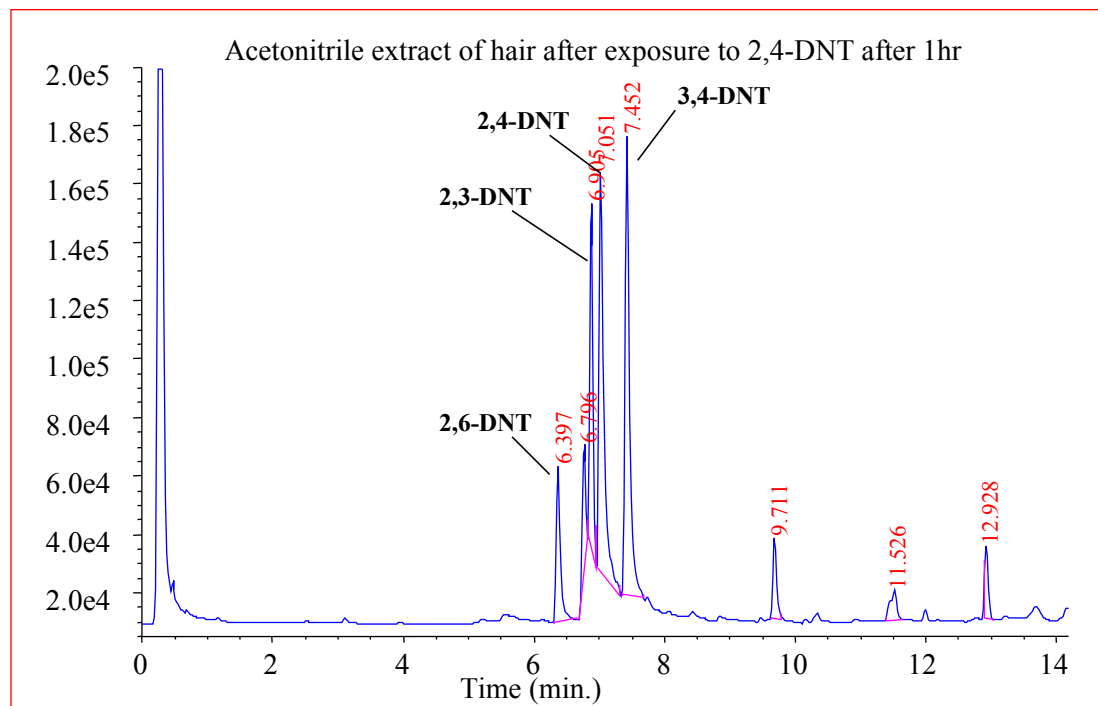


Figure 5. Chromatogram of acetonitrile extract of hair after 1hr exposure to 2,4-DNT