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Accumulation of Explosives in Hair

ABSTRACT: The sorption of explosives (TNT, RDX, PETN, TATP, EGDN) to hair during exposure to their vapors is examined. Three colors of hair were simultaneously exposed to explosive vapor. Following exposure of hair, the sorbed explosive was removed by extraction with acetonitrile and quantified. Results show that sorption of explosives, via vapor diffusion, to black hair is significantly greater than to blond, brown or bleached hair. Furthermore, the rate of sorption is directly related to the vapor density of the explosive: EGDN > TATP $\ggg$ TNT $\gg$ PETN > RDX. In some cases, the explosive-containing hair was subject to repeated washings with sodium dodecylsulfate or simply left out in an open area to determine the persistence of the explosive contamination. While explosive is removed from hair with time or washing, some persists. These results indicate that hair can be a useful indicator of explosive exposure/handling.

KEYWORDS: forensic science, TNT, RDX, PETN, TATP, EGDN, hair, explosive sorption, explosive vapor

There is considerable evidence that drugs, metals and other chemicals are assimilated into hair as a result of ingestion and metabolic activity (1). This study documents the sorption to hair of explosives in the vapor phase. Since the mid-1900's researchers have been examining hair of laboratory animals and humans as evidence of exposure to chemicals (2–5). Hair has been shown to sorb heavy metals, pesticides, drugs (illicit and prescription), nicotine, and other chemicals which contaminate the environment (Table 1), but illicit drug detection appears to generate the most interest. While analysis of body fluids, i.e., blood and urine, provide unequivocal evidence of drug use, these methods are invasive. Furthermore, the elimination time is short; abstinence of only a few days reduces concentrations of drugs and their metabolites in body fluids to below detectable limits. In contrast, hair has been shown to retain drugs and their metabolites for many weeks following abstinence. The Society for Forensic Toxicology has accepted drug analysis of hair as a confirmatory technique, and the Substance Abuse and Mental Health Administration reviewed various factors pertinent to use of this technique as legal evidence (6,7).

Hair testing has the advantages of being non-invasive, able to provide a historical record of exposure, resistant to countermeasures, and may offer a wider window of detection than analysis of body fluids (8–10). These advantages are evident from the suggestion that applicants for re-instatement of their driver's license in the province of Brescia, Italy be required to submit hair samples as proof of sustained abstinence from cocaine and heroin (11). Despite the advantages, there remains much controversy concerning detection of drugs in hair as evidence of drug usage. In addition to the presence of drugs and drug metabolites in the hair matrix that result from illicit use, drugs can be present after passive exposure (8). There is also evidence that assimilation is related to hair color and race (12–17). Hair color in humans and laboratory animals (rats and monkeys) appears to influence the extent to which drugs are sorbed, with dark hair picking up more than light hair. This is evident in a study where the subjects (rats) had both black and white hairs. The black hairs assimilated significantly more methadone than white (12). A number of studies have attempted to elucidate the sorption processes associated with the binding of drugs to hair. There is convincing evidence that drug-binding sites are associated with melanin granules, but the importance of other factors, such as hair lipid content, is a matter of some debate. One hypothesis is that hydrophobic interactions involving lipids binding non-polar organic substrates to hair play an important role (18–22). Hair is composed of complex micro-environments and mechanisms by which it associates or assimilates substances are unclear. In this study the authors prefer to use the term "sorption" instead of more definitive terms such as "adsorption" or "absorption" to describe the interactions of explosives with hair because specific mechanisms by which explosives associate with hair have not been ascertained.

The use of hair as evidence of exposure to explosives was pioneered by Wardleworth and Ancient of Royal Airforce Research and Development Establishment (RARDE), now British Defense Scientific and Technical Laboratory (dstl). They showed that nitrobenzene and ethylene glycol dinitrate (EGDN), both liquids with high vapor pressures, sorbed to bulk hair (23). With researchers at dstl, we initiated a preliminary study to evaluate the feasibility of detecting common military explosives in hair. Most military explosives are solids with very low vapor pressures. That study showed that both 2,4-dinitrotoluene and 2,4,6-trinitrotoluene (TNT, the most common filler of landmines) were readily sorbed by hair (24).

The contamination of hair with explosives can occur by several modes—the interaction with explosive vapor, direct contact with explosive particles, or secondary contact involving direct transfer of particles from hands to hair. The study reported herein examined contamination of hair via vapor interaction only. This mode of exposure was chosen as a benchmark because it could be performed without the use of human subjects. Cut hair could be acquired by purchase or donation. A complimentary study is underway at dstl to examine particulate transfer to scalp hair of human subjects (The presence of explosive contamination is assessed by swabbing the hair with combs threaded with specially prepared gauze or cotton.). To examine explosive transfer to hair by vapor

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TABLE 1—*Chemicals known to be sorbed to hair.*

Chemical Substances
amphetamines
barbiturates
benzphetamine & its metabolites
cannabinoids
cocaine, benzoylecgonine & other metabolites
codeine & acetylcodeine
DDT
dextropropoxyphene & norpropoxyphene
diazepam
ephedrine
heroin
Malaoxon
Malathion
methadone and its metabolites
methylenedioxymethylamphetamine (Ecstasy)
morphine & acetylmorphine
nicotine
nordiazepam
ofloxacin
oxazepam
pentobarbital
phencyclidine (PCP)

contact only, weighed quantities of hair were suspended over explosive powder. Four colors of hair were examined—black, brown, blond and bleached—though the majority of the studies focus on the first three. Five explosives were used—2,4,6-trinitrotoluene (TNT); hexahydro-1,3,5-trinitro-s-triazine (RDX, the active ingredient in C4); pentaerythritol tetranitrate (PETN, the explosive found in detonating cord and sheet explosives); ethylene glycol dinitrate (EGDN); and triacetone triperoxide (TATP, a homemade explosive recently figuring in a number of terrorist incidents). These explosives represent a broad range of volatilities. The sorption isotherms of TNT on the different colored hairs are reported. In addition, the persistence of explosive contamination on hair over time and after treatment with detergent was examined.

Experimental Section

Exposure of Hair to Explosives

Amber, glass, wide-mouth, screw-cap jars (10.5 cm diameter × 8.5 cm high) were washed with soap and water, rinsed with acetone, oven dried, and cooled to room temperature in a desiccator. Approximately, 0.5 g of explosive was placed in the bottom of the jar. Hair tresses, obtained from various sources, were washed by repeated rinsing with sodium dodecylsulfate. Each hair color was removed from its plastic storage bag with forceps, placed on clean paper, and cut into about 1.5–2.5 cm lengths with scissors. About 100 strands of this hair (~0.3 g) were positioned on weighing paper (ends folded), weighed, and transferred to an aluminum foil weighing boat 1.5 cm in height and 6 cm in diameter. Three of these containers ("baskets") were strung vertically on an aluminum wire so that they would stack into the wide-mouth jar one above the other with sufficient space for air/vapor circulation. Generally, the oriental hair was in the top basket; the brown hair in the middle; and the blond hair in the bottom. During handling, care was taken that no contact was made between hair and other objects, particularly contact with the solid explosive on the bottom of the jar. The jars were stored in a fume hood in the laboratory, and the samples were incubated for various intervals.

Quantification of Explosives Sorbed to Hair

At the completion of the exposure time, the tier of baskets was removed from the explosive-exposure jar, and each hair type was placed on clean waxed paper where it was spread out and fluffed to mix inside and outside fibers. Each hair color was then divided into three portions of about 0.1 g each. Each portion, three for each of the three hair colors, was weighed into an amber, 16 mL, screw-cap bottle. None of the hair strands was allowed to touch the lid of the bottle. Acetonitrile (5.00 mL) was added, and the samples were sonicated for 20 min before they were placed on a shaker (speed 86 shakes/min) for overnight extraction. After extraction, the acetonitrile was removed using a Pasteur pipette and about 1 mL of this solution was put in a 2 mL, septum screw-cap gas chromatograph (GC) vial (Initially, solution was filtered prior to placement in the vials; however, this step was later deemed unnecessary). The acetonitrile extracts were analyzed on a Hewlett Packard (HP) 5890 or an Agilent 6890N gas chromatograph (GC) using an electron capture detector (ECD) or micro-ECD, respectively. The column used was a J&W Scientific DB-5MS column [8 m × 0.53 mm (megabore), film 1.5 μm] (HP) or a HP-5 (20 m × 0.25 mm, capillary column, Agilent). Details, including the injector and detector temperatures, initial and final oven temperatures, hold times and ramp rates, are shown below in Table 2. An external standard method was used to quantify extracted samples. Known concentrations of explosives were prepared in HPLC grade solvent (usually acetonitrile) and analyzed via GC or LC. Standard curves of area and height versus concentration for each explosive were constructed (using 5 points between 0.01 and 1.0 ppm). The correlation coefficients for the standard curves were better than 0.99. Both height and area data gave comparable results. The peak heights and/or areas for acetonitrile extracts of hair were used to extrapolate concentrations from the appropriate separately prepared standard curve. From the concentration and volume of extract plus mass of hair extracted, and it was possible to determine mass of explosive sorbed per gram of hair (μg/g). EGDN sorption was determined using high pressure

TABLE 2—*GC analysis conditions.*

Sample	Split/Splitless	Sample Volume (μL)	Injector Temperture (°C)	Detector Temperture (°C)	Oven Temperture (°C)	Hold Time (sec)	Ramp Rate (deg/min)	Final Temperature (°C)	Final Hold Time (min)	Retention Time (min)
PETN hair	split 5:1	1	175	250	50	60	20	200	5	7.7
RDX hair	split 12.5:1	1	195	320	50	60	10 to 200 C, 20	250	5	15.5
TATP hair	split 125:1	1	165	300	50	120	20	220	0.5	5.5
TATP vapor@	split 125:1	10	165	300	50	120	20	280	2	6
TNT vapor@	split 5:1	10	165	300	50	120	20	280	2	10
TNT hair*	splitless	1	175	325	60	30	15	200	10	7

* Analyses performed on HP 5890 GC with DB-5MS column; all others used Agilent 6890N with HP-5 column.

liquid chromatography (HPLC). Analysis of 5 μL samples was with a Hypersil BDS-C18 column (4.0 × 100 mm, 3-micron) and a mobile phase of 40% methanol in water. Quantification at 214 nm was with a photodiode array detector.

Persistence of Explosive in Hair

Experiments described above show that hair sorbs explosive vapor. However, questions of retention are important to any potential forensic applications. These issues were addressed with several types of explosive-exposed hairs. Explosive-contaminated hair was divided into three portions (~0.1 g each), and one or two portions were immediately analyzed to confirm the amount of explosive sorbed. The other portions were treated in one of the following ways. To examine persistence of the explosive in hair over time, portions of the hair were placed on clean watch glasses and allowed to stand in an explosive-free office (i.e., static air flow) for at least 2 days prior to analysis. The persistence of explosive upon washing of hair was evaluated as follows. A portion of the hair (~0.1 g) was placed in 100 mL beakers with ~0.5 mL of 2% SDS solution. The mixture was stirred well with a glass rod. After a little water (~5 mL) was added, the foam was decanted, and the procedure was repeated. The hair was then rinsed three times until no foam was visible. The hair was dried and extracted with acetonitrile as described above.

Results and Discussion

Sorption versus Position in Jars

The baskets in the jars were different distances form the solid explosives. To determine whether ordering of the hair in the baskets made a difference, blond hair was placed in all three baskets and exposed to TATP for 24 h. Results were similar to within experimental error (Table 3).

Sorption versus Amount of Hair

Four explosives were pure powders: TNT, PETN, RDX, TATP and one, EGDN, was a liquid. To determine whether the amount of hair in each basket affected the results, two exposure chambers were prepared in which each basket contained only a third as much hair (about 0.1 g) as was usually used. The results were similar to within experimental error, indicating reproducibility, and in correct proportion to hair exposed in 0.3 g portions for comparable periods of time.

TABLE 3—*Blond hair exposed to TATP 24 h.*

	μg/g Hair	Average μg	Std. dev.
Top	47.8		
Top	59.6		
Top	69.7	59.0	10.9
Middle	51.9		
Middle	47.4		
Middle	42.3	47.2	4.8
Bottom	49.6		
Bottom	51.0		
Bottom	60.4	53.7	5.9

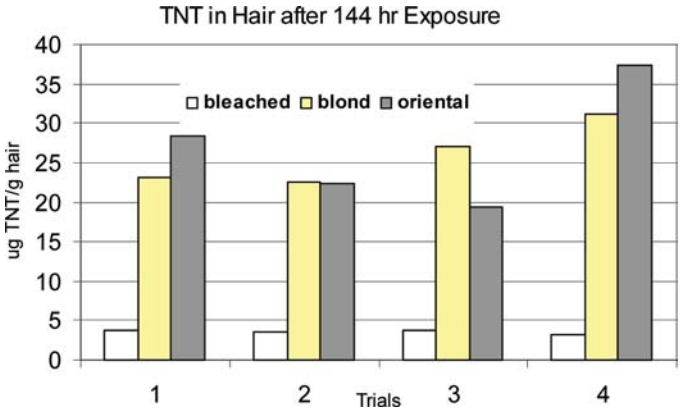

FIG. 1—*TNT uptake by hair.*

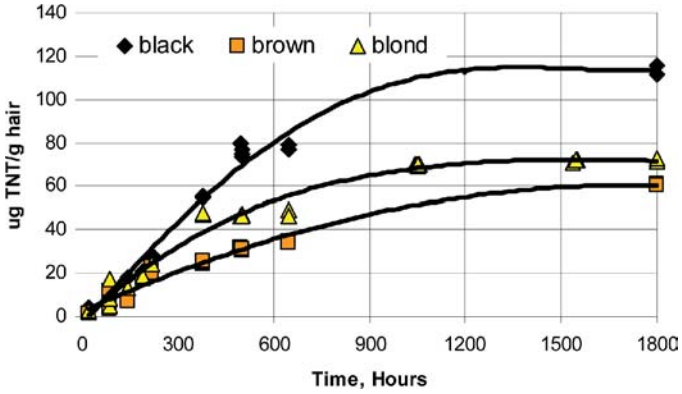

FIG. 2—*Sorption of TNT by black, brown, & blond hair over time.*

Sorption Versus Chemical Composition of Explosive

The literature reports that the occurrence of drugs in hair by users may be related to color. Our initial studies used black, blond and bleached hair. We found, like for drugs, that the black hair sorbed more chemical (in this case, TNT) than blond while bleached hair sorbed the least TNT (Fig. 1). Three colors of hair, black (oriental), brown, and blond were exposed to TNT vapors for varying amounts of time in an attempt to determine at what concentration the hair was saturated. Table 4 shows micrograms of TNT observed on average of three runs for 10 time intervals. When these data are plotted (Fig. 2), it appeared that the hair was nearing saturation at 1800 h (75d). For the brown and blond hair, sorption of TNT reached a maximum of ~60 and 70 μg per gram hair, respectively, after about 1000 hours. In contrast, black oriental hair contained greater than 100 μg of TNT per gram hair and this was still

TABLE 4—*TNT Sorbed to Hair μg TNT/g Hair (GC Analysis by Area). Standard deviations are indicated in parentheses.*

hair\hours	24	std dev	91	std dev	144	std dev	192	std dev	220	std dev	380	std dev	500	···	504	std dev	648	std dev	1800	std dev
oriental	4.2	0.4	13	2.0	18	0.2	20	0.1	28	0.1	55	0.5	80	···	75	1.6	79	1.3	114	3.0
brown	1.4	0.0	7.2	4.1	7.4	0.2	17	0.2	21	1.3	25	0.7	32	···	31	0.3	34	0.5	61	0.1
blond	2.4	0.2	10	6.6	13	0.1	19	0.4	24	0.1	48	0.5	46	···	47	0.6	48	1.4	72	0.5
bleached					3.6															

TABLE 5—*PETN (μg)/g hair.*

hair\hours	1848	2376	5040
oriental 1	60	100	103
oriental 2	59	97	103
brown 1	24	37	59
brown 2	24	37	60
blond 1	34	38	75
blond 2	36	39	75

TABLE 6—*RDX (μg)/g hair.*

hair/hours	768 h	5808 h
oriental	5.6	7.6
oriental	5.6	7.1
brown	1.6	2.1
brown	1.6	2.3
blond	2.0	2.6
blond	2.0	2.7

increasing after 1000 h. Much longer exposure times than those used for TNT were needed before significant quantities of PETN or RDX were detected. Table 5 indicates that in 5040 h (~7 months) the micrograms of PETN sorbed approached the same levels observed for the three colors of hair for TNT after 75 days. Table 6 shows that RDX sorption was substantially less; about 7 μg/g hair (oriental) and about 2 μg/g hair (brown and blond) after 5808 h. Our hypothesis was that saturation levels of hair were comparable for every explosive, but the rates of achieving saturation were dramatically different. A different type of explosive, TATP, was used to test this hypothesis. The uptake of TATP was prompt and much more extensive. The apparent plateau of 100 μg per gram black hair for the NO_2 functionalized explosives (TNT, RDX, PETN) was not observed for TATP (Table 7). TATP readily sorbed over 1000 μg/g for black (oriental) hair within 48 h. We reasoned that the high vapor pressure of TATP was related to the high rate of sorption. EGDN is a NO_2 functionalized explosive with a relatively high vapor pressure. Table 8 indicates that sorption rate for EDGN was ~21000 μg/g for black (oriental) hair in 48 h. Clearly, vapor pressure is an important, perhaps dominant criterion, for sorption of explosives to hair under the experimental conditions used in this study.

Effect of Vapor Density on Sorption

Vapor pressure data were available for TNT, RDX, PETN, and EGDN, but none had been reported for TATP. To further investigate the relationship between vapor pressure and sorption to hair, we determined the vapor pressure of TATP. The vapor density of TATP in sealed containers, equilibrated at specified temperatures, was determined by injecting known volumes of vapor into a gas chromatograph with electron capture detection. Assuming ideal gas behavior, it was possible to calculate the vapor pressure. Vapor pressures were measured as a function of temperature and a Clapeyron plot, constructed. Details have been reported elsewhere (25). The vapor density of TNT was measured at the same time to confirm the applicability of the protocol used to determine the vapor pressure of TATP. The value determined for TNT was in agreement with those reported in the literature (Table 9). Thus, we have confidence in the value measured for TATP–0.03 mm at 25°C. Figure 3 illustrates time dependent uptake of various explosives. Not surprisingly

TABLE 7—*TATP (μg)/g hair.*

hair\hours	48	240
oriental 1	1061	1673
oriental 2	1080	1681
oriental 2	1096	
brown 1	38	92
brown 2	37	84
brown 3	38	
blond 1	58	199
blond 2	55	201
blond 3	53	

TABLE 8—*EGDN (μg)/g hair. The Demeo Brown hair (for scientific purposes) was purchased from Demeo Brothers, NY.*

	1 h	48 hx
Chinese Black	418	21404
	410	22143
	407	...
Demeo Brown	709	12433
	666	12479
	679	14030
Blond	433	18493
	528	14188
	403	...

TABLE 9—*Values for TNT and TATP vapor pressure.*

A	B	mm Hg 25°	Pa at 25°	ΔH_{sub} (kJ/mol)	TNT Reference	
TNT						
...	...	5.80E-06	7.73E-04	...	Hobbs	1986
12.31	5175	8.97E-06	1.17E-03	...	Pella	1977
19.23	7371	3.22E-06	4.11E-04	...	Legget	1977
15.43	6180	5.04E-06	6.56E-04	118	Edwards	1950
12.6	5900	5.66E-06	7.50E-04	113	Cundall	1978
8.754	4227	3.77E-06	5.25E-04	81	Oxley	this work
TATP						
17.666	5708	3.32E-02	4.33	109	TATP	this work

where $\log_{10} P(\text{mmHg}) = A\text{-}[B/T(K)]$.

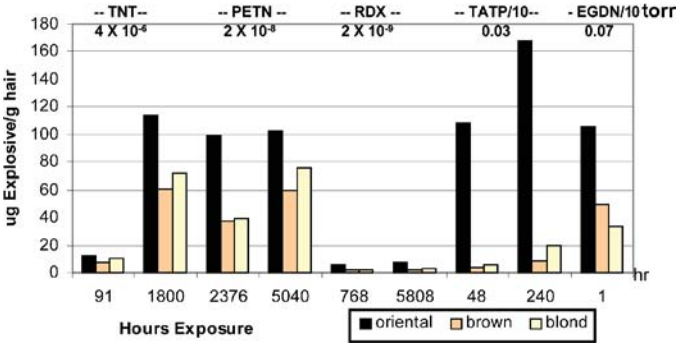

FIG. 3—*Sorption of various explosives vs. time (TATP & EGDN values were divided by 10).*

rate of sorption appears directly related to available vapor of the explosive (room temperature vapor pressures in parentheses):

$$\text{EGDN}\ (0.07) > \text{TATP}\ (0.03) \gg \text{TNT}\ (4 \times 10^{-6})$$

$$\gg \text{PETN}\ (2 \times 10^{-8}) > \text{RDX}\ (2 \times 10^{-9}).$$

TABLE 10—*Persistence.*

	TATP	EGDN	TNT	PETN
Hours Exposed	48	48	1800	5040
ug/g oriental	1346	21400	114	103
ug/g brown	65	12981	61	60
ug/g blond	71	16341	72	75
	% Retained on Standing in Air 48 h			
black	15%	11%	100%	...
brown	28%	31%	98%	...
blond	11%	31%	97%	...
	% Retained on 3 Washes of 2% SDS			
black	81%	44%	40%	5%
brown	59%	10%	69%	2%
blond	75%	24%	43%	2%

Percent of explosive retained is relative to the μg of explosive (per gram hair) of the sample after exposure to explosive but before standing or washing (shown in upper table).

The foregoing analysis presupposes that explosive vapors reach equilibrium with the solid within a short time. Various experiments, such as the similarity of uptake with different size samples (*vide supra)* or different size of containers, have convinced us that this is true.

Persistence of Explosives in Hair

It was found that after standing in an explosive-free environment or being washed hair still retained a detectable amount of explosive (Table 10). Those with the highest vapor pressures, TATP and EGDN, were preferentially lost on standing. TNT, with a relatively low vapor pressure, was almost completely retained on standing, but significantly depleted upon washing. Since high retention in air was also expected with PETN, only the washing test was performed.

Conclusion

This study shows that hair is a viable surface from which explosive traces can be recovered. While contamination of hair may come by contact with explosive vapor or by particulate transfer—direct or indirect (e.g., hands transfer to hair), this study specifically examined vapor transfer. It showed that even explosives with extremely low vapor pressure (i.e., RDX) may be sorbed by hair. The sorbed explosive persists on the hair. Simply standing in air, TATP, EGDN and TNT remained on hair up to two days; and TNT, up to six days. (Six days was the maximum standing time allowed since it was assumed after six days, head hair would be washed.) It is likely that similar persistence in air will be observed for PETN and RDX. A more rigorous test of persistence is washing. Though explosive sorbed by hair was susceptible to removal during washing, laboratory washings showed that some explosives persisted through up to three (TATP, EGDN, PETN) and six (TNT) rinses. Since frequency and mode of hair washing varies dramatically among individuals, there is the possibility that explosive residues will persist in hair for days after exposure. Preliminary results from the dstl Forensic Explosive Laboratory with subjects who handle explosives suggest that particulate transport is even more significant than vapor deposition. Indeed some workers, who reportedly washed their hair after a day of exposure to explosives, were still found contaminated the following day.

The shapes of the curves in Fig. 2 suggest an adsorption mechanism for describing the interaction of TNT vapor with hair. However, hair is a complex matrix consisting of myriad microenvironments. These preliminary results do not provide sufficient evidence for us to fully speculate on mechanisms of interaction between explosives and hair.

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