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Tunable, Self-curing Polymers for the Forensic Collection of Latent Signatures from Within Porous Materials

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Abstract— Self-curing polysiloxane polymers have been developed for the forensic collection of latent signatures of explosives, organophosphates, and chemical warfare agent (CWA) degradation products. These polymeric materials penetrate the sample substrate as viscous liquids and subsequently harden to a semi-soft solid that can be peeled away from the substrate to extract signatures via the non-covalent interaction of the newly formed polymeric material with the analytes buried within the substrate. This paper discusses experiments aimed at altering the chemical and physical properties of the polysiloxane sampling materials to optimize signature recovery from porous substrates. The utility of this approach is demonstrated by the collection of target analytes from within concrete. The recovery of these signatures using the self curing polymeric formulations is compared to current operational sampling alternatives such as adhesive fingerprint lifters and swabs. Demonstration of the preparation, extraction, and analytical methods for the detection of the target analytes is also presented.

Keywords— polymers; explosives; organophosphates; pesticides; LC-MS; GC-MS.

I. INTRODUCTION

Efficient recovery of high value signatures from porous surfaces (e.g., concrete, brick, and stone) presents a unique challenge as existing collection technologies do not adequately probe the pores, cracks, and crevices of these materials [1]. The porosity of these materials may allow for extensive absorption and concentration of chemical signatures below the surface of the material. This property presents not only a challenge to adequately recover these latent signatures, but also an important and underutilized sampling opportunity. While relatively uniform and non-reactive surfaces such as glass and counter tops are often a good choice for sample collection, there are many cases in which these exposed surfaces have undergone environmental changes or cleaning prior to the sampling event. This perturbation often results in alteration, reduction, or complete removal of the once prevalent chemical signatures. In these cases, highly porous materials may offer an extremely important sampling alternative, but only if they can be exploited efficiently.

This operational need is being addressed through the development of a collection technique using self-curing polysiloxane polymers [2, 3]. In this case, these materials were specifically formulated to retrieve chemical signatures from within porous substrates by designing them to adequately penetrate a porous surface and harden to a semi-soft solid that can be subsequently peeled away from the substrate, thereby extracting signatures buried within the material via the non-covalent interactions between the target analytes and the newly formed polymer. The collection materials are comprised of two components: 1) the Base Paste, which consists of vinylsiloxanes capable of undergoing crosslinking reactions with hydrosiloxane components, and 2) the Catalyst Paste, which contains a catalytic component that initiates the hydrosilylation reaction involving the addition of the hydrogen atoms bonded to silicon atoms across the vinyl groups [2-5]. In addition, each component also contains retarders that influence the onset of polymerization, surfactants that improves the wettability of the polymer, fillers to add bulk to the material, and other additives to influence various physical properties [2]. Table I summarizes the components of the polysiloxane polymers developed in this study.

TABLE I. FORMULATION OF THE BASE AND CATALYST PASTES

Component	Formulation
Base Paste	<ul style="list-style-type: none">• Hydrosiloxanes• Vinylsiloxanes• Fillers• Additives
Catalyst Paste	<ul style="list-style-type: none">• Catalysts• Vinylsiloxanes• Fillers• Additives

In the present study, we have exploited these polymerizable polyorganosiloxanes to recover representative explosives such as trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), triacetone triperoxide (TATP), and pentaerythritol tetranitrate (PETN) (selected

structures shown in Fig. 1), as well as organophosphates and pesticides (dimethyl methylphosphonate (DMMP), fonofos, mephosfolan, malathion, parathion, and a CWA degradant, 4,4 oxide 1,4-oxathiane, structures shown in Fig. 2) from porous concrete surfaces. The utility of these materials is further demonstrated by comparing the extraction efficiencies of the polysiloxane materials to conventional operational sampling devices, in this case cotton swabs and adhesive fingerprint lifters. Successful development and rapid transition of this novel sampling system (along with associated preparation and analysis methods) to field applications could result in a transformational technology that augments the capabilities of anyone concerned with the recovery of high value signatures for explosives, toxins, and biological threat agents.

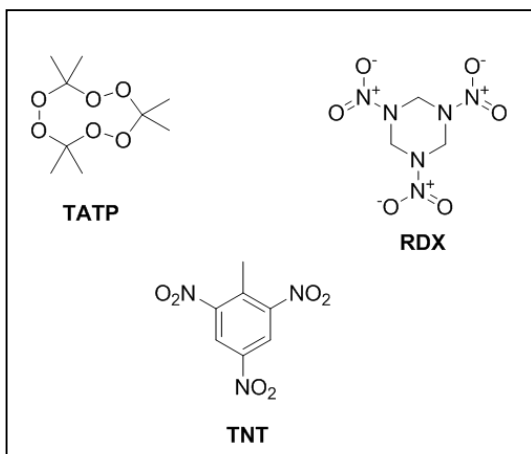


Figure 1. Structures of the Explosives Analytes

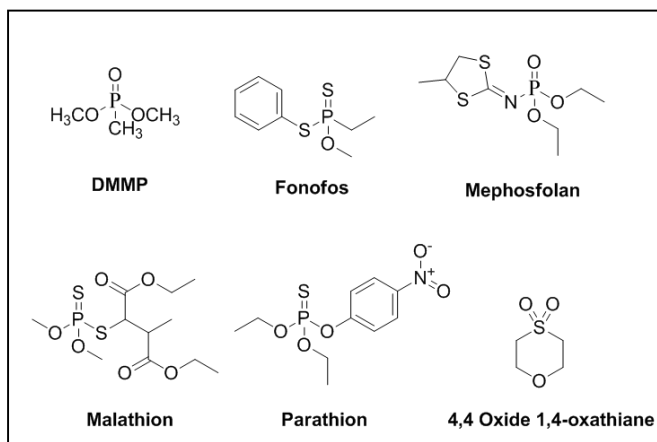


Figure 2. Structures of the Organophosphate and Pesticide Analytes

II. EXPERIMENTAL

A. Extraction Studies

A 0.5 mL aliquot of a 500 ppm solution of each analyte was spiked onto a controlled area of a concrete surface and allowed to dry. For each analyte, three parallel surfaces were spiked to enable side-by-side extraction by a prototype polysiloxane polymer, an adhesive fingerprint lifter, and a

cotton swab. For extractions using the polymer, the material was applied to the concrete surface and allowed to cure for approximately 10 min. The polymer was then peeled off the surface and extracted with 5 mL of acetonitrile.

The surfaces were sampled by the adhesive fingerprint lifters by applying the adhesive side to the concrete surface and applying pressure to ensure sufficient contact was made over the entire sampling surface. The lifter was then peeled off the surface and extracted with 5 mL of acetonitrile. Extractions using the cotton swab were performed by brushing the swab across the concrete surface for approximately 5 sec. The cotton tip was then removed and placed in a vial. A 5 mL aliquot of acetonitrile was added to the vial, which was then sonicated for 10 min. The supernatant was then transferred to a clean vial for analysis.

Due to requirements in the analytical method, a solvent exchange to ethyl acetate was performed prior to analysis of solutions containing DMMP, fonofos, mephosfolan, malathion, parathion, and 4,4-oxide 1,4-oxathiane. The final solutions from all three extraction methods were diluted 1:1 (v/v) using a solvent suitable for the analysis method. Samples containing RDX and PETN were diluted with water, those containing TNT and TATP were diluted with acetonitrile, while those containing DMMP, fonofos, mephosfolan, malathion, parathion, and 4,4-oxide 1,4-oxathiane were diluted with ethyl acetate.

B. Analysis Methods

1) HPLC-MS/MS Analysis

RDX and PETN were quantified in extracts by HPLC-MS/MS using a Thermo Fisher Surveyor HPLC coupled to a Thermo Fisher TSQ triple quadrupole mass spectrometer. Separation was achieved using a reversed-phase, XBridge C₁₈ column (2.1 x 50 mM, 5 μm) and a gradient program with mobile phase comprised of 0.25 mM ammonium nitrate in water (mobile phase A) and 0.25 mM ammonium nitrate in acetonitrile (mobile phase B). The initial conditions of 100% A were held for 3.0 min, and then the composition was linearly ramped to 50% A/50% B over 17.0 min. The gradient was then changed to 30% A/70% B over 5.0 min, followed by an additional ramp to 5% A/95% B over 5.0 min. The mobile phase was returned to initial conditions in 1.0 min, followed by a 10.0 min re-equilibration time. Detection was by mass spectrometry using negative mode electrospray ionization (ESI) with a spray voltage of -4.0 kV and sheath and auxiliary gas flow rates of 50 and 20 arbitrary units (corresponding to approximately 0.75 L/min and 6 L/min), respectively. The temperature of the heated inlet capillary was set to 200 °C. The selected reaction monitoring (SRM) scan mode was used and the analytes were quantified using an external standard calibration curve.

2) GC-MS Analysis

TATP, TNT, DMMP, fonofos, mephosfolan, malathion, parathion, and 4,4 oxide 1,4-oxathiane were analyzed using GC-MS. Experiments involving TNT were executed on an

Agilent 7890/5975 GC MS equipped with a PTV inlet. The method utilized an RTX-5MS capillary column (15 m x 0.25 mm id, 0.25 μ m stationary phase thickness) and a temperature program to separate the analytes. The column oven was held at an initial temperature of 75 $^{\circ}$ C for 0.6 minutes, ramped at 8 $^{\circ}$ C/min to 175 $^{\circ}$ C, ramped at 6 $^{\circ}$ C/min to 240 $^{\circ}$ C, ramped at 40 $^{\circ}$ C/min to 320 $^{\circ}$ C and held for 2 minutes. Splitless injection was performed using a PTV inlet heated to 25 $^{\circ}$ C for 0.5 min and then ramped at 720 $^{\circ}$ C/min to 250 $^{\circ}$ C and held for 2 minutes. Detection was by electron ionization (EI) MS. Target analytes were identified by comparison of the analyte mass spectrum to that of a standard prepared from reference standards. The analytes were quantified relative to an internal standard using a calibration curve. TATP samples were analyzed on a Thermo Focus DSQ II single quadrupole GC-MS equipped with an RTX-5MS capillary column (15 m x 0.25 mm id, 0.25 μ m stationary phase thickness). Splitless injection at 110 $^{\circ}$ C was used with the following temperature program: the column oven was held at 50 $^{\circ}$ C for 3 minutes, ramped at 8 $^{\circ}$ C/min to 180 $^{\circ}$ C and held for 3 minutes. The mass spectrometer was operated in the full scan mode for detection. TATP was quantified using a calibration curve generated with a reference standard.

Experiments involving DMMP, fonofos, mephosfolan, malathion, parathion, and 4,4-oxide 1,4-oxathiane were executed on an Agilent 7890A/5975C GC-MS equipped with a split-splitless inlet. The method utilizes a Restek Rxi-5sil capillary column (30 m x 0.25 mm id, 1 μ m stationary phase thickness) and a temperature program to separate the analytes. The column oven was held at an initial temperature of 45 $^{\circ}$ C for 3 minutes, ramped at 8 $^{\circ}$ C/min to 121 $^{\circ}$ C, ramped at 16 $^{\circ}$ C/min to 145 $^{\circ}$ C, ramped at 8 $^{\circ}$ C/min to 237 $^{\circ}$ C, ramped at 30 $^{\circ}$ C/min to 310 $^{\circ}$ C and held for 10 minutes. Splitless injection was performed using a split-splitless inlet heated to 250 $^{\circ}$ C. Helium was used as a carrier gas at a flow rate of 2 mL/min. Detection was by MS using EI. The target analytes were identified by comparison of the analyte mass spectrum to that of standards, and quantified relative to an external calibration curve.

III. RESULTS AND DISCUSSION

A. Development of Tunable Self-Curing Polymer Formulations

Initial experiments were aimed at developing a polymer formulation that was optimized for the collection of explosives, organophosphates, pesticides and CWA degradation products from porous substrates. One key advantage of these polymers is their tunability. By altering the formulation of the base and catalyst components, the material properties of the polymer, such as cure time, viscosity, tear strength and surface interaction, can be altered to best suit the sampling need. Table 2 summarizes the attributes identified to have the greatest impact on the sampling capability of the polymers and the components of the formulation affecting each attribute.

TABLE II. KEY POLYMER MATERIAL PROPERTIES AND RELATED FORMULATION COMPONENTS

Material Property	Related Formulation Component
Cure Time	<ul style="list-style-type: none"> Amount of catalyst Presence of retarder Amount of filler Degree of crosslinking
Viscosity	<ul style="list-style-type: none"> Amount of fillers Viscosity of formulation components used Type of additive(s) used
Tear Strength	<ul style="list-style-type: none"> Amount of filler Degree of crosslinking Molecular weight of the individual components in the formulation (higher initial molecular weight gives higher strength product) Inclusion of quadrifunctional resin (Q-resin)
Surface interaction	<ul style="list-style-type: none"> Surfactant influences how the polymer interacts and thus binds analytes on a surface

Selected formulations from the extensive refinement study are shown in Table 3. Due to the proprietary nature of the investigation, the specific components of each formulation are not detailed, however the critical material properties for porous sampling using the prototypes is shown. In addition to the properties shown in the table, the thixotropy attribute of the polymers was also minimized to allow the material to flow into the pores and crevices of the surface without the application of force to “flatten out” the polymer. This characteristic increases the reproducibility of the application and sampling, while enhancing the ease of use and minimizing the risk of cross contamination. Based on the results of the optimization study, formulation MR-32 was found to have the most desirable materials properties and was subsequently used for further extraction efficiency studies.

TABLE III. SELECTED FORMULATIONS FOR THE MATERIALS PROPERTIES OPTIMIZATION STUDY

Formulation	Cure Time	Viscosity	Tear Strength	
SC-28	Moderately quick	High	Good	
CM-17	Very slow	High	Low	
MB-23	Very slow	Very low	Very low	
SS-12	Too slow	Good	Low	
LP-58	Very slow	Low	Very low	
JC-21	Very fast	Very high	Very low	
CH-38	Good	Moderately high	Low	
CM-92	Good	Good	Good	
LP-64	Moderately slow	Moderately high	Low	
MB-84	Very fast	Very high	Very low	
SS-01	Very slow	Very high	Very low	
SC-65	Good	Moderately low	Good	
HB-017	Good	Good	Good	
HB-65	Good	Moderately low	Moderately low	
MG-58	Very fast	Very high	Low	
LB-38	Very fast	Very high	Low	
CM-13	Good	Good	Ideal	
SC-65	Good	Good	Ideal	
MR-32	Good	Ideal	Ideal	
JC-87	Good	Good	Good	
Key to Polymer Material Properties				
Very undesirable	Undesirable	Moderate	Desirable	Ideal

B. Extraction Studies

To evaluate the extraction capability of the self-curing polymer formulations in comparison to conventional techniques, a known amount of various explosives was spiked onto concrete and collected by the polymer, an adhesive lifter, and a cotton swab. Samples were extracted from the polymer, lifter, and swab using acetonitrile and analyzed by GC-MS or LC-MS to identify and quantify the amount of explosive material collected.

Representative results of the extraction efficiency studies are shown in Figures 3 and 4. In initial studies, three early polymer formulation prototypes, LB-28, MB-42, and HB-40 were tested against a conventional adhesive fingerprint lifter for the extraction of TATP. Figure 3 demonstrates that all three of the self-curing polymers were able to extract TATP, while the conventional lifter was not.

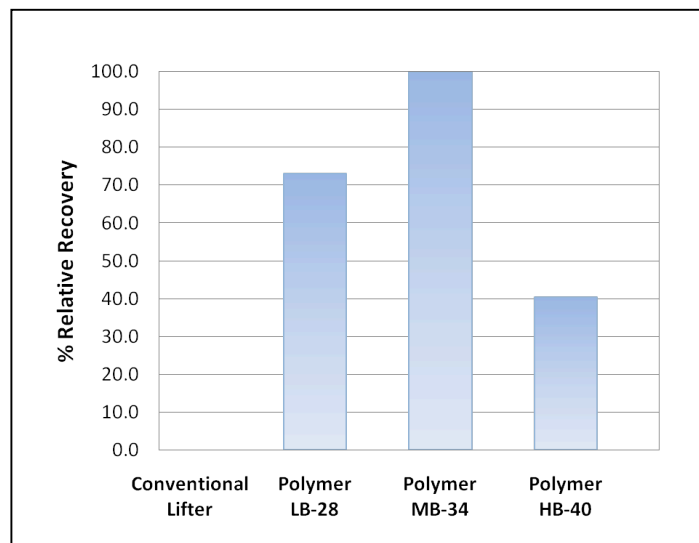


Figure 3. Relative recoveries of TATP from concrete using prototype formulations compared to a conventional finger print lifter.

The properties of MB-34 were further optimized in the refinement study to yield the MR-32 formulation. Figure 4 demonstrates that MR-32 was able to extract TNT from concrete while the conventional swab and lifter did not show any recovery for the analyte. Similarly, the polymer extracted a significantly greater amount of RDX and PETN from a concrete surface than a conventional adhesive lifter and the cotton swab. These results highlight the potential for improved trace level collection of explosive compounds using the self-curing polymers compared to conventional sampling materials employed in both portal screening and forensic field collections.

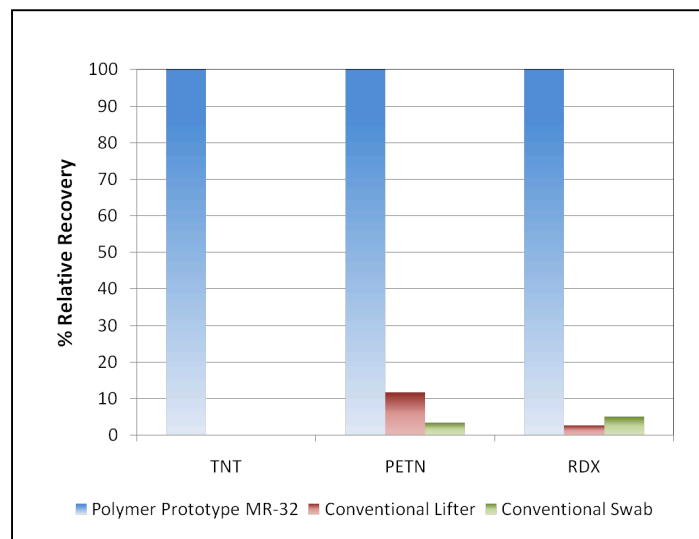


Figure 4. Relative recoveries of TNT, PETN, and RDX from concrete using the refined polymer formulation (MR-032) compared conventional adhesive fingerprint lifters and a cotton swabs.

The extraction efficiency of the polymer compared to the adhesive lifter and cotton swab for organophosphates, including DMMP, fonofos, mephosfolan, malathion,

parathion, and a CWA degradant, 4,4 oxide 1,4-oxathiane spiked onto concrete was also evaluated. Samples were extracted from the polymer, adhesive lifter, and swab using acetonitrile and analyzed by GC-MS.

Results of these studies are highlighted in Figure 5 for DMMP, fonofos, and mephosfolan, and Figure 6 for malathion, parathion, and 4,4 oxide 1,4-oxathiane. Similar to the results for the experiments involving the explosive compounds, these data clearly demonstrate that the MR-032 polymer formulation recovered a significantly greater amount of each target analyte from the concrete. In some cases, the conventional materials were unable to recover any of the target analyte, as seen with the extraction of DMMP and mephosfolan using the cotton swab. The recoveries of DMMP, malathion, and parathion using the swab and adhesive lifter, and 4,4 oxide 1,4-oxathiane using the swab, were nearly an order of magnitude lower than those achieved using the polymer. Moreover, it is likely that the conventional materials only recovered residual analyte that remained on the surface of the concrete, while the polymer recovered more analyte by penetrating the pores of the concrete. On-going studies are aimed at demonstrating the utility of the polymers after the surface has been cleaned.

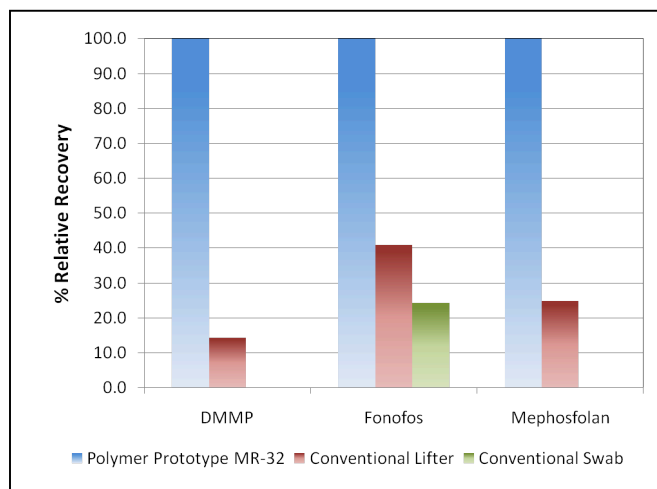


Figure 5. Relative extraction efficiencies of DMMP, fonofos, and mephosfolan using the polymer formulation MR-32 compared conventional adhesive fingerprint lifters and cotton swab.

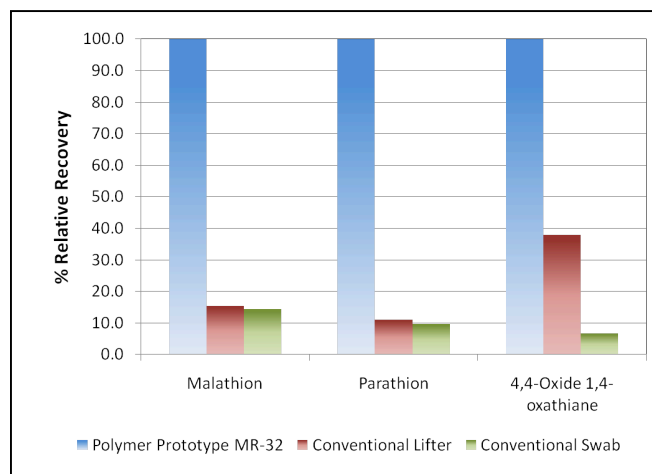


Figure 6. Relative extraction efficiencies of malathion, parathion, and 4,4-oxide 1,4-oxathiane using polymer formulation MR-32 compared to conventional adhesive fingerprint lifters and cotton swabs.

IV. CONCLUSION

Self-curing polyvinylsiloxane polymers are a promising alternative to conventional adhesive fingerprint lifters and cotton swabs for the collection of trace levels explosives, organophosphates, pesticides, and CWA degradation products from porous surfaces. The material properties of the polymers can be easily tuned through manipulation of the formulation, and extensive studies have been performed (and are on-going) to optimize these materials for the collection of these and other latent signatures from concrete and other porous and non-porous surfaces. The ability of these polymers to probe the cracks and crevices of porous material will ultimately enhance collection efficiencies and bolster the capability of forensic collectors.

The success of these initial studies highlights the promise of additional work. In planned studies, the collection protocols, sample preparation and analysis methods will also be optimized to continue to improve collection and extraction efficiencies, and ultimately reduce the level of detectable contamination. In addition, new polymer formulations specifically designed for extracting other target analytes, such as biological threat agents, DNA and other analytes of forensics interest will be performed.

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