Polycyclic Aromatic Hydrocarbon Release from Pavement Rejuvenators Due to Rolling Wheel Contact: An Investigation Using a Model Mobile Load Simulator

by

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ABSTRACT

Polycyclic aromatic hydrocarbon (PAH) compounds, which are common to coal tar and coal-tar-based products, are ubiquitous environmental contaminates with carcinogenic effects to human health and aquatic life. Transport of PAHs via solid phase particulate motion, gaseous phase volatilization, and aqueous phase dissolution into urban waterbodies of PAH compounds from coal-tar-based pavement sealant products has been studied. Pavement rejuvenators are products applied to increase the usable life of pavement. Coal-tar-based rejuvenators contain a significantly larger mass fraction of coal-tar with respect to coal-tar-based sealants, but pavement rejuvenators have not been as extensively studied as pavement sealants.

Chemical analysis of detached pavement material treated with coal-tar-bases, asphalt-based, and bio-based rejuvenators was conducted with gas chromatography – mass spectrometry (GC/MS) analysis for 16 PAH compounds and two aromatic heterocyclic organic compounds following extraction with methylene chloride. Detached pavement material was collected from 19 simulated asphalt surface abrasion experiments that used a model mobile load simulator (MMLS) test apparatus that replicated surface challenges from vehicular traffic. The MMLS test apparatus configuration allowed asphalt disc samples treated with different rejuvenation products, to be tested and for detached material to be collected and quantified prior to GC/MS analysis.

Test cases evaluated the influence of rejuvenation product type and cure time, as well as the effect of sand application (simulating sand application during slippery winter storm conditions) had on detached particulate and ultimate PAH compound loading. The average mass of particulate detachment from samples following a 48 hour cure time, for the asphalt-based and coal-tar-based rejuvenator products were 0.347 g and 0.480 g, respectively. This mass of detached material was lower than that from pavement treated with bio-based rejuvenator and the control (not treated), which had 4.858 g and 2.567 g of detached particulate material, respectively. When the product cure time was increased to three weeks, which was significantly long enough to capture effects of compound volatilization, average particulate detachment increased to 0.882 g for the coal-tar-based rejuvenator and decreased for the bio-based rejuvenator to 2.600 g. Six tests performed with a single application of winter storm sand after a 48 hour product cure time showed an increase in average particulate detachment to 1.450 g and 0.617 g for pavement treated with the asphalt-based and coal-tar-based rejuvenators, respectively. Conversely, under the same conditions, a reduction in average detached particulate to 3.749 g was observed for the bio-based product.

Detached particulate material quantities for each test case were used with the respective cumulative concentration of 16 PAH compounds quantified to make an assessment on the potential PAH compound contamination via solid phase particle transport. The average PAH compound concentration in particulate detached from pavement treated with a coal-tar-based rejuvenator was 3062.8 mg PAH per kg of particulate. This was an order of magnitude higher than the average PAH concentration measured in particulate detached from the two control pavement samples and the two asphalt-based samples after a 48 hour cure time, which were 322.1 and 508.1 mg PAH per kg detached particulate, respectively. PAH compound concentrations were also normalized by the surface area of pavement treated with a rejuvenator to determine the potential PAH compound contamination per unit area. Normalized results for each rejuvenator type were averaged to make an overall evaluation of the potential rejuvenator specific PAH compound loading. The coal-tar-based, bio-based, and asphalt-based rejuvenators had a normalized cumulative solid-phase PAH compound release of 2.35, 0.88, and 0.17 mg PAH per square foot of pavement rejuvenated, respectively. In addition, carbazole was quantified in all pavement samples treated with the coal-tar-based rejuvenator at an average concentration of 125.6 mg carbazole per kg detached particulate. Acridine was quantified in detached particulate from five of seven coal-tar-based test performed at an average concentration (excluding non-detection samples) of 42.1 mg acridine per kg detached particulate.

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1.0 Introduction

The mobilization and transport of polycyclic aromatic hydrocarbon (PAH) compounds into the environment through association with particulates (Van Metre et al. 2009; Baldwin et al. 2016), volatilization (Van Metre et al. 2012), and dissolution into storm water discharge (Maher, Van Metre and Foreman 2014; Watts et al. 2010) has been researched, and a linkage has been established to PAH contamination of local water resources and the use of coal-tar-based pavement sealant products. Mobilized PAH compounds have adverse effects on aquatic life and human health, with 16 PAH compounds identified as priority pollutants by the United States Environmental Agency (EPA). Similar to pavement sealants, pavement rejuvenators are intended to extend the service life of asphalt pavements such as roadways and parking lots (Boyer 2000). Rejuvenators, like sealants, can be derived from asphalt, bio-base, or coal-tar base materials.

Coal-tar-based rejuvenators have a higher mass-fraction of coal tar than coal-tar-based sealants (see Appendix A), however research into the mobilization and transport of PAH compounds from coal-tar-based rejuvenators to the surrounding environment is limited. Two separate undergraduate research projects at Worcester Polytechnic Institute (WPI) have collected detached pavement surface material (MacDonald and Meyer, 2017) and simulated pavement surface material detachment (Barr et al. 2018) from pavement treated with a coal-tar-based rejuvenator to evaluate solid phase concentrations of PAH compounds in the detached particulate material. Barr et al. 2018 also evaluated the concentration of PAH compounds in particulate detached from pavement treated with asphalt-based and bio-based rejuvenators. Van Metre et al. in 2009, and separately the University of New Hampshire Stormwater Center in 2010, chemically analyzed dust samples collected from asphalt parking lots where coal-tar-based sealants were applied. Results from Barr et al. 2018 indicated the quantity of PAH compounds contained in abraded surface particles from asphalt treated with a coal-tar-based rejuvenators is similar to, if not greater than, that from coal-tar-based sealants.

The present study evaluated solid phase transport of 16 PAH and two aromatic heterocyclic compounds via particulate detached via repeated tire contact from pavement surfaces treated with coal-tar-based, asphalt-based, and bio-based rejuvenation products. A quantitative assessment of the potential environmental loading each rejuvenation product type posed was made based on the total analyzed PAH and aromatic heterocyclic compound concentrations measured in quantified detached pavement material. Parameters that affect pavement surface abrasion were controlled and conditions that were hypothesized to have a significant influence on the total PAH compound loading from rejuvenated pavement particulate were assessed. Included was the cure time each rejuvenation product had prior to vehicular traffic and the influence of a sand application (typical of a slippery winter storm conditions).

2.0 Background

A continuous need in the transportation industry to maintain and preserve asphalt pavement is driven by the significant cost to resurface existing pavement relative to the cost of commercially available pavement preservation techniques (Brownridge, 2010). Despite proven release of PAH compounds from coal-tar-based sealants and initial finding of solid phase PAH transport through particle detachment from coal-tar-based rejuvenators, as discussed below in Section 2.1, many municipalities and transportation agencies still depend on coal-tar-based preservation products to maintain asphalt surfaces and slow the effects of asphalt degradation (discussed in Section 2.3).

As discussed in Section 2.2, the physical and chemical properties of different PAH compounds vary. As such multiple simultaneous transport mechanisms, which can be dependent on compound type, occur. However, transport through particle detachment and further physical transport mechanisms is relevant for all PAH compounds present in coal-tar-based pavement products. Therefore, particle detachment and subsequent motion was the primary transport mechanism consider in this work. As mentioned above in Section 1.0, pavement exposure to common winter storm sand application (discussed in Section 2.4) may exacerbate particle detachment and subsequent PAH compound transport, and therefore was also evaluated.

2.1 PAH Compound Release from Coal-Tar-Based Pavement Preservation Products

Subsequent PAH compound transport through particle abrasion and detachment from asphalt surfaces treated with coal-tar-based sealants has been studied. One of the first published research programs that assessed PAH compound transport from pavement coated with coal-tar-based sealants was conducted in Austin, Texas (City of Austin, 2005). Elevated levels of PAH compounds were found in streambed sediment samples collected adjacent to parking lots. Streambed sediment sample investigation revealed abraded asphalt surface material, amongst other pollutants, from an adjacent parking lot which had a coal-tar-based sealant applied. Subsequent dust samples were then collect from various other parking lots that had been treated with coal-tar-based sealants, asphalt based sealant, and some parking lots that had not treated at all. Collected dust/particulate samples were chemically analyzed following EPA guidelines. The total PAH compound concentration measured in samples collected from parking lots treated with coal-tar-based sealants were multiple orders of magnitude higher than in samples collected from parking lots treated with similar asphalt-based sealants, or not treated at all. The minimum, maximum, and median total PAH compound concentrations measured from all processed dust samples collected from parking lot surfaces treated with a coal-tar-based sealants in this study (City of Austin, 2005), as well as other studies discussed below, are presented in Table 2-1.

Table 2-1: Measured PAH Compound Concentration from Parking Lot Dust Samples

Source	**Median PAH [mg PAH /kg Dust]**	**Min PAH [mg PAH /kg Dust]**	**Max PAH [mg PAH /kg Dust]**
City of Austin, 2005	2100	250	13050
Van Metre, Mahler, and Wilson 2009	2200	Not Available	Not Available
Watts et al. 2010	Not Available	266	1192
Mahler et al. 2010	4760	387	11300
Baldwin et al. 2016	Not Available	622	908

In a subsequent 2009 study, Van Metre et al., collected parking lot dust samples in nine different United States cities and analyzed the samples for PAH compounds. Cities were geographically selected for regional data population to assess trends in PAH concentration measured in collected samples. Their results showed higher occurrence of coal-tar-based sealer use on parking lots located in central and eastern cities with respect to western cities. This correlated with elevated PAH compound concentrations measured in parking lot dust samples collected from central and eastern locations. Watts et al. 2010, Mahler et al. 2010, and Baldwin et al. 2016 also measured elevated PAH compound concentrations in dust samples collected from parking lots treated with coal-tar-based sealant, as shown above in Table 2-1. In the studies referenced above, dust samples collect and analyzed for PAH compounds from unsealed parking lots or parking lot treated with non-coal-tar-based products, exhibited significantly lower PAH compound concentration with respect to dust samples collected from parking lots treated with coal-tar-based sealers.

In 2017, MacDonald and Mayer collected surface samples form an asphalt road located in a low traffic volume residential area that had been treated with a coal-tar-based rejuvenator. Collected samples were analyzed for 16 PAH compounds by gas chromatography (GC). The average measured PAH concentration for the collected surface samples was 8,225 mg PAH/kg solid which was higher than all median PAH compound concentrations measured from parking lot dust collected from pavement treated with coal-tar-based sealers (see Table 2-1). Higher PAH compound concentrations measured collected surface material from coal-tar-based rejuvenators is intuitive as the mass fraction of coal-tar in coal-tar-based pavement rejuvenators is larger than that in coal-tar-based sealants, as discussed in Appendix A.

Barr et al. 2018 measured PAH compound concentrations in material detached from asphalt pavement treated with one of three types of rejuvenation products under simulated vehicular traffic; coal-tar-based, asphalt-based, and bio-based. The study used a Model Mobile Load Simulator (MMLS) test apparatus to provide continuous and controlled tire surface abrasion to six inch diameter asphalt sample discs. For each experiments asphalt pavement sample discs were treated with one of three rejuvenation products. The test apparatus allowed detached pavement material resultant from tire abrasion to be collected, quantified, and then separately chemically analyzed for 16 PAH compounds via methylene chloride extraction and GC analysis. Particulate material detached from the samples treated with the coal-tar-based rejuvenator contained higher concentrations of PAH compounds with respect to samples treated with asphalt-based or bio-based rejuvenators, and samples that had not been treated (control). A summary of the result in terms of PAH compound concentration per mass of detached material and the mass of detached material per test are shown in Table 2-2.

Table 2-2: PAH Compound Concentrations in Detached Rejuvenator Particulate (Barr et al. 2018).

Asphalt Surface Treatment	Detached Particulate PAH Concentration [mg PAH /kg detached material]	Mass of Detached Material [g]
Asphalt-Based Rejuvenator	364	0.8315
Bio-Based Rejuvenator	582	0.5559
Coal-Tar-Based Rejuvenator	3440	0.2458
No Rejuvenator	1510	0.2259

In addition to transport via mobilization via solid phase, gaseous phase PAH compound transport from asphalt pavement surfaces treated with coal-tar-based sealcoats has been assessed. In 2012 Van Metre et al. measured volatilization rates from asphalt immediately after application, and during subsequent days (up to one year) after the application of a coal-tar-based sealant. Changes in the measured PAH compound volatilization rates near the treated pavement surface were fit to an ln-regression model that showed a decrease in the first two weeks after product application. Pavement surface scrapings were obtained at the location volatilization measurements were made and were analyzed for PAH compound concentrations. Measured PAH compound concentrations in the pavement scraping also showed a decline in PAH compound concentration with respect to the time after the sealant was applied. Based on their experimental data they estimated an approximate 25 to 50 percent loss in PAH compounds in the coal-tar sealant, based on sealant scrapings, during the first sixteen days after application.

2.2 Characteristics of PAH Compounds

PAH compounds are a group of aromatic hydrocarbons that differ in molecular size based on the number of benzene rings present in the molecule (Abdel-Shafy and Mansour 2016). The chemical properties of PAH compounds vary, particularly with respect to water solubility and volatility, and are dependent on specific compound molecular weight, among other molecular properties. PAH compounds with lower molecular weight tend to be more volatile and water soluble. PAHs are also soluble in organic solvents which are used for extraction from solid phases.

PAH compounds are generally classified based on formation into two general categories. PAHs are either petrogenic or pyrogenic, meaning they were formed at low temperature over geologic time scales or at high temperature on rapid time scale, respectively (Abdel-Shafy and Mansour 2016). Pyrogenic PAHs are often from man-made point sources and therefore are an environmental concern. The formation of pyrogenic PAH compounds occurs during the incomplete combustion of carbon-based material such as wood, petroleum, and coal. Among other processes that produce PAHs, a PAH rich byproduct may be formed when coal is coked to produce the feedstock for steel production (Ahrens and Depree 2010). The byproducts of coked coal production are coal tar and coal-tar pitch, which are used as the base material for pavement rejuvenators.

PAH compounds and coal tar are problematic to aquatic life and human health. Coal tar and coal tar pitches, both found in coal-tar-based pavement rejuvenators, have been identified as Group 1 carcinogens, meaning there is sufficient evidence to show carcinogenic effects in humans, by the International Agency for Research for Cancer (American Cancer Society). Furthermore, the EPA has identified 16 PAH compounds, which are listed below in Table 2-3 along with their respective chemical formula and molecular weight, as priority pollutants (US EPA 2014). With respect to aquatic life, PAHs have been proven to cause fin erosion, liver abnormalities, cataracts, skin tumors, and immune system impairments in fish and inhibited reproduction, delayed emergence, and mortality in organisms that live on the bottom of stream beds such as benthic macroinvertebrates (Eisler, 1987).

Table 2-3: Sample PAH Compound Properties

Compound	Chemical Formula	Molecular Weight [g/mol]	Compound	Chemical Formula	Molecular Weight [g/mol]
Acenaphtene	$C_{12}H_{10}$	154.212	Dibenz(a,h)anthracene	$C_{22}H_{14}$	278.354
Acenaphthylene	$C_{12}H_8$	152.196	Fluoranthene	$C_{16}H_{10}$	202.256
Anthracene	$C_{14}H_{10}$	178.234	Fluorene	$C_{13}H_{10}$	166.223
Benz(a)anthracene	$C_{18}H_{12}$	228.294	Indeno(1,2,3-c,d)pyrene	$C_{22}H_{12}$	276.338
Benzo(a)pyrene	$C_{20}H_{12}$	252.316	Naphthalene	$C_{10}H_8$	128.174
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.316	Phenanthrene	$C_{14}H_{10}$	178.234
Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.338	Pyrene	$C_{16}H_{10}$	202.256
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.316	Carbazole*	$C_{12}H_9N$	167.211
Chrysene	$C_{18}H_{12}$	228.294	Acridine*	$C_{13}H_9N$	179.222
Perylene-d12	$C_{20}H_{12}$	264.389			

* Indicates aromatic heterocyclic compounds included in subsequent chemical analysis but are not PAH compounds or priority pollutants

2.3 Asphalt Pavement Aging and Rejuvenation

Asphalt rejuvenation products are applied to increase the service life and reduce long term ownership costs of asphalt pavement (Brownridge, 2016). To establish how a rejuvenation or a seal coat product extends pavement service life, asphalt pavement formation, characteristics, and the aging process must be established.

Asphalt pavement mixtures are broken down into two principle components, aggregate and binder. Aggregate is the bulk component of an asphalt concrete. Aggregate is a coarse, inorganic material which chemically does not change or degrade over the pavement lifespan. Binder, also known as bitumen (for asphalt pavement), is the asphalt component of asphalt concrete that holds the aggregates together to form the pavement structure. Asphalt binder is comprised predominately of complex mixtures of organic compounds which can vary significantly between batches of asphalt (Boyer 2000).

The fundamental process of asphalt aging is ubiquitous; upon atmospheric oxygen exposure the organic oily compounds within the asphalt start and continue to oxidize (Boyer 2000; Islam 2015; Peterson 1984). The large variation in chemical makeup of asphalt makes detailed chemical characterization of asphalt mixtures, and the subsequent oxidation process, difficult. Therefore, various fractionalized approaches to more generally characterize the organic compounds of asphalt into categories that could be used to predict pavement behavior and aging have been developed. The three common approaches for characterization are partitioning with selective solvents (uses increasingly polar solvent to remove fractions of decreasing polarity), selective adsorption-desorption, and chemical precipitation; processes which were developed by Schweyer and Traxler, Corbett, and Rostler and Sterberg, respectively (Peterson 1984; Rostler and White 1960).

The approach established by Rostler and Sternberg can be used to show the effects of oxidation on the chemical makeup of asphalt and can be a gauge for how a rejuvenator is intended to function. This approach uses solvents to separate asphalt components into the categories of organic molecules shown schematically below. As seen in Figure 2-1, after the first separation process asphalt is sub-divided into asphaltenes (shown on the left) and maltens (all the components shown on the right), which are the hard, brittle, insoluble components and the oily resins of asphalt, respectively (Brownridge 2016; Peterson 1984). The ratio of asphaltenes and maltens is crucial to maintain a flexible pavement structure as excessive asphaltenes would result in brittle pavement. However, as asphalt oxidizes the maltens convert to asphaltenes. The oxidation processes is further complicated as the each component of the maltens group oxidizes at a different rate with the nitrogen bases reacting most rapidly with each subsequent component reacting at a slower rate (Boyer 2000).

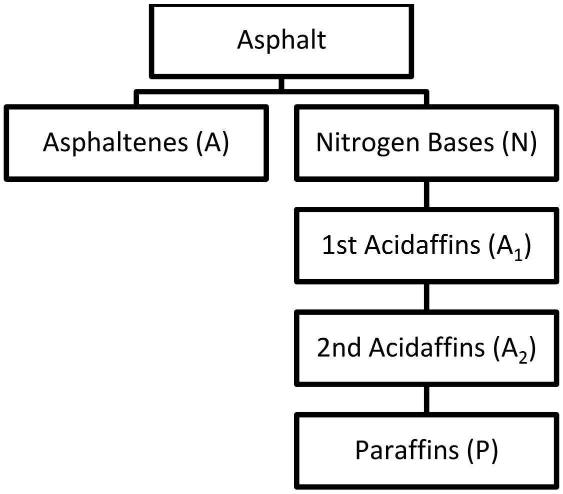

Figure 2-1: Rostler & White Analysis (Petersen 1984).

Pavement rejuvenation or seal coat application are used to reverse or protect against increased ratios of asphaltenes to maltens caused by oxidation. Regardless of the base material (coal-tar, asphalt, or bio-based) sealant emulsions are applied to the pavement surface to seal voids to prevent oxygen form reacting with binder below the surface. Asphalt rejuvenation products address asphalt oxidation by replenishing oxidized maltens. Rejuvenators, which were first introduced to the transportation market with an asphalt based product in 1960 by the Golden Bear Oil Company (Brownridge, 2010), that was intended to penetrate beyond the pavement surface to restore the original properties of the binder.

2.4 Application of Sand for Skid-Resistance during Winter Ice/Snow Storms

Sand is an anti-skid material applied for slippery conditions during winter storms to improve traction by increased friction between automobile tires and snow covered roadways (Nikon 2001). The use of anti-ski materials such as winter storm sand have been widely implemented and as such recommended practices with respect to the type and quality of anti-skid material, and their rate of application exist.

Anti-skid material can be categorized by the type and gradation of abrasive used. Per the Pennsylvania Department of Transportation (PennDOT) 2016 construction specification, anti-skid material is classified into one of the four following categories; Type AS1 which is either a natural or manufactured sand, Type AS2 and AS3 which are made from crushed stone or crushed gravel with the main difference being the respective grain size distributions, and Type AS4 which is derived from crushed slag. For each category PennDOT established acceptance criteria for the material which include bulk density and gradation. For Type AS1 sands the required bulk density must be between 70 and 110 lbm/ft^3. The required gradation

AS1 sands are provided below in Table 2-4 below. It should be noted that not all values were specified as indicated by blank spaces in the table below.

Table 2-4: Anti-Skid Material Gradation Requirements

Anti- Skid Type	Maximum Percent Passing Sieve						
	1/2"	3/8”	No. 4	No. 8	No. 50	No. 100	No.200
Type AS1		100	60-100	0-80		0-8	0-5
Type AS2		100	35-80	0-45		0-6	0-3
Type AS3	100	90-100		0-30		0-8	
Type AS4		100		0-30		0-8	0-5

The application rate of sand is important to its effectiveness as an anti-skid material and is generally reported in units of mass of sand per lane mile, which equates to the mass of sand applied to a 12 foot wide lane for one mile (LRRB 2012; Gonsalves 2012). Per the 2005 Minnesota Snow and Ice Control Handbook when winter sand use is recommended, based on temperature and weather conditions, the sand application rate should be between 250 and 375 pounds per lane mile.

3.0 Hypotheses and Objectives

The following hypotheses for this research were developed based on the background information established above;

- Older, oxidized asphalt that is brittle will yield a higher particulate detachment rate from tire abrasion, even when treated with a coal-tar-based, asphalt-based, or bio-based rejuvenator, in comparison to new asphalt with the same surface treatment. As such the subsequent total PAH contaminate mobilized from a pavement per unit area will be higher as asphalt age increases.
- Detached particulate material caused by tire abrasion on asphalt treated with a coal-tar-based rejuvenator will have a lower concentration of PAH compounds if the rejuvenation product had a longer cure time prior to tire abrasion as a result of PAH compound volatilization.
- The application of winter storm sand will increase friction and tire abrasion between the pavement and automobile tires and therefore the subsequent particulate detachment from pavement treated with a rejuvenation product will increase.
- Coal-tar-based rejuvenators will have higher total PAH contaminate mobilization from the treated pavement per unit area compared to bio-based and asphalt based rejuvenators.

Thereby the following objectives were derived;

- Determine the mass of detached pavement material following the application of coal-tar-based, bio-based, and asphalt based pavement rejuvenation products resultant from pavement surface challenges that include tire and sand abrasion.
- Determine the concentration of PAH compounds and aromatic heterocyclic hydrocarbon compounds in detached pavement material.
- Determine the influence of rejuvenator cure time on particulate detachment from pavement surface challenges and subsequent compound loading.

4.0 Experimental Methods

The experimental approach evaluated solid phase mobilization of 16 PAH compounds and two aromatic heterocyclic hydrocarbon compounds via rejuvenated pavement surface particulate detachment. Pavement samples were treated with coal-tar-based, bio-based, or asphalt-based rejuvenation products and subjected to replicated surface challenges in a controlled, consistent manner with a model mobile load simulator (MMLS) test apparatus (see Section 4.2). The test apparatus provided continuous tire contact to six inch diameter pavement sample discs and controlled tire velocity and contact pressure two parameters that affect pavement particle detachment. This test apparatus allowed variations in the mass of detached pavement material and the respective compound concentration per mass of detached material to be attributed to parameters evaluated.

Based on the hypotheses established above, the rejuvenation product type (coal-tar-based, asphalt-based, and bio-based), the time duration after product application, and effects of a single sand application (typical of a winter storm event) were evaluated with respect to solid phase PAH compound transport. Portions of the experimental approach were designed similar to that taken by Barr et al. 2018 such that an assessment on the effect asphalt age, at the time of rejuvenation product application, could be made with respect to solid phase PAH transport.

A test began with sample disc preparation for the MMLS test apparatus. Core samples were taken from one location, cut to the geometry compatible with the MMLS sample fixtures, and the application of a rejuvenation product (Section 4.3). Following the required cure time, sample discs were subjected to tire abrasion within the test apparatus followed by the collection, quantification, and chemical analysis of all detached pavement material from test case.

Chemical analysis of detached pavement material focused on 16 PAH compounds identified by the US EPA as priority pollutants, as shown above in Table 2-3, as well as acridine and carbazole. Chemical analysis was done with a methylene chloride extraction followed by GC/MS analysis (Section 4.5). All chemical analysis and particle detachment test results area presented in Section 5.0.

4.1 Test Matrix

The type of rejuvenation product applied to the pavement sample disc prior to surface abrasion was evaluated by all test cases. In total, three different rejuvenation products were used; a coal-tar-based, an asphalt-based, and a bio-based rejuvenator. It should be noted here that the asphalt based product was not strictly a rejuvenator but had similar properties of asphalt-based rejuvenators.

As stated above in Section 3.0, it was hypothesized that the duration of time a rejuvenation product had to penetrate and cure on a pavement surface prior to renewed vehicular traffic would affect both particle detachment as well as the concentration of PAH compounds contained within those detached particles. Two different product cure times with a time sufficient time separation to capture possible change in PAH compound concentration contained in detached surface particles, as a result of rapid initial surface volatilization, particularly for the coal-tar-based product, were used. The first was a short duration cure time of 48 hours. The short cure time was previously used by Barr et al. 2019 and would thereby allow direct comparison to their test results, if used. The 48 hour cure time was selected as it bound the minimum cure times recommended for each of the product types used. The second, longer duration cure time, was nominally set at three weeks to exceed the point (16 days) when initial volatilization was anticipated to rapidly decrease, as discussed above in Section 2.1.

Two control tests with no rejuvenation product applied to the samples were performed to provide a baseline for both compound loading and detached particulate mass. All the test cases including product type, cure time, and the number of each test respective test case preformed are shown below in Table 4-1. Also included in Table 4-1 are six tests that evaluated sand abrasion effects which are further discussed in Section 4.4.

Table 4-1: Abrasion Test Matrix

Rejuvenator Type	Rejuvenator Cure Time	Winter Sand Application	Number of Tests
Control – No Rejuvenator	N/A	No	2
Coal-Tar-Based	48 Hours	No	3
Coal-Tar-Based	48 Hours	Yes	2
Coal-Tar-Based	3 Weeks	No	2
Asphalt-Based	48 Hours	No	2
Asphalt-Based	48 Hours	Yes	2
Bio-Based	48 Hours	No	2
Bio-Based	48 Hours	Yes	2
Bio-Based	3 Weeks	No	2
Total Number of Abrasion Tests			19

4.2 Simulated Tire Abrasion Test Procedure

All test cases used a Model Mobile Load Simulator (MMLS) test apparatus to replicate solid phase PAH compound mobility though pavement detachment resulting from pavement surface challenges (continuous tire abrasion). The MMLS test apparatus, shown below in Figure 4-1, consisted of five tires located on a conveyor track system that continually contacts, in this instance, circular pavement sample discs. The MMLS test apparatus had user defined operational settings that controlled the one directional tire travel velocity over the asphalt sample discs as well as the contact force between the five tires and the pavement discs. Consistent tire travel velocity was monitored with a cycle counter that tracked the number cycles completed by the MMLS conveyor system over the known test duration.

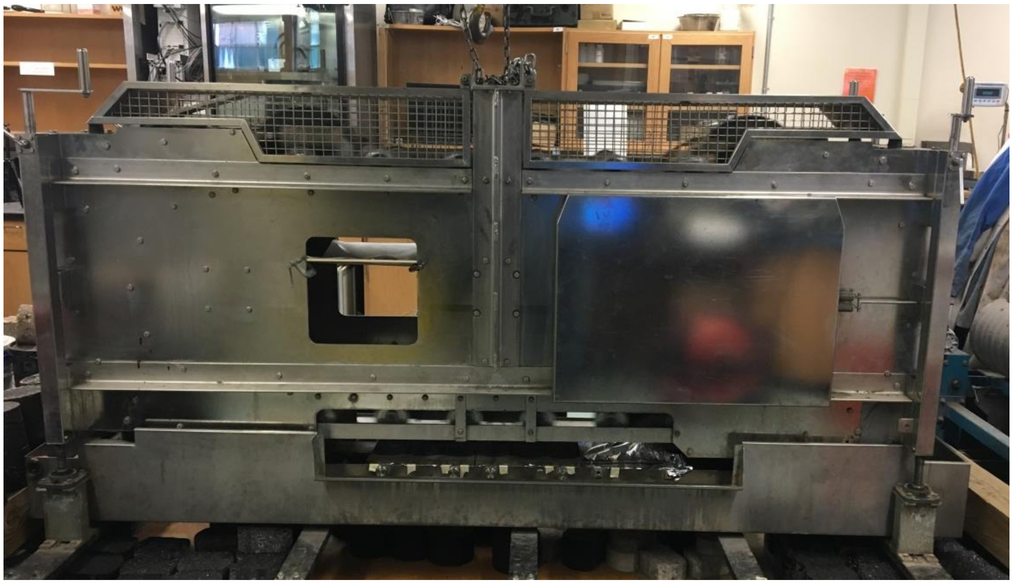

Figure 4-1: MMLS Test Apparatus

The MMLS test apparatus was used to simulate a consistent, repeated surface contact resulting in material detachment that could be repeated for all tests. Solid phase PAH compound loading and rejuvenator performance relative to each product type based on particulate detachment are not dependent on the exact operating conditions so long as they were constant for all tests. Therefore, for all tire based abrasion tests both the travel velocity, as tracked by the number of cycles completed in a defined period of time, and contact forces were held constant.

For test result comparison to Barr et al. 2018, which utilized the same MMLS test apparatus used herein, the operation parameters for all tests were selected to be similar to those previously implemented. Per Barr et al. the target number of cycles in a 24 hour period ranged from approximately 78,700 to 81,400. The contact force previously used was undocumented and could not be confirmed the same. However contact force adjustment required height manipulation of the four legs that support the MMLS apparatus, which was unlikely as the test apparatus had only been used for a lab demonstration since Barr et al. completed their work.

Within the MMLS test apparatus nine modified circular asphalt samples (see Section 4.3 for sample disc preparation) could be installed. To prevent detached material travel around and dropout into the mechanical components of the MMLS the final three discs were intentionally omitted to provide a location for the majority of detached material to accumulate. Prior to the pavement sample disc instillation the entire lower region of the MMLS was vacuumed cleaned. An aluminum foil liner was also installed in the internal chamber that housed the pavement test discs to assist in the collection of detached material. Asphalt discs installed in the MMLS as well as the aluminum foil liner can be seen if Figure 4-2 below.

At test termination the aluminum foil liner was cut and removed after the last test disc taking care not loose detached material. Once removed the top surfaces of each test disc, the regions of the MMLS adjacent to the test discs, and locations not lined with aluminum foil were vacuumed with a Dirt Devil® hand-held vacuum to collect detached particulate material. Prior to use the collection chamber and filter assembly of the hand held vacuum was soaked in and thoroughly cleaned with Citranox® acid cleaning detergent, rinsed with warm tap water, rinsed a minimum of two times with reagent grade water, and allowed to dry. Asphalt discs were only removed once all detached material had been collected. Any material found between or beneath sample discs after removal was considered a test artifact and not included in the mass of detached material because the majority of this material, if any was observed, detached from the edges of discs during removal.

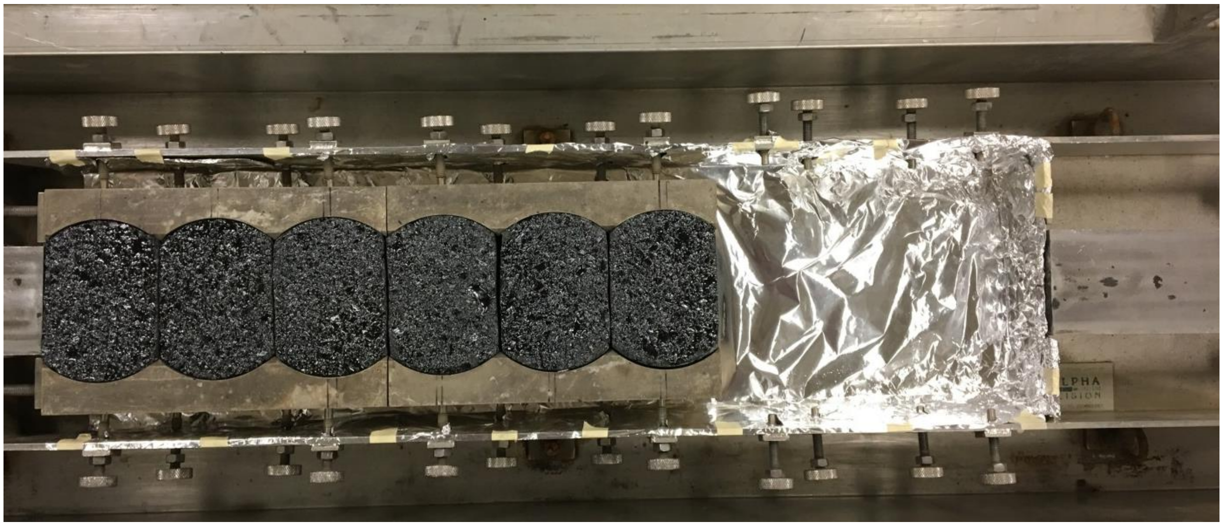

Figure 4-2: Asphalt Discs Installed in MMLS with Aluminum Foil Liner

Collected detached particulate was transferred from the removed aluminum foil, the hand held vacuum collection chamber, and the vacuum filter to a clean sheet of aluminum foil. The new sheet of aluminum foil was used transfer particulate into a clean (see Section 4.6 for the glassware cleaning procedure used), pre-weighed glass vials with screw top lids. Visual inspection of the collected material from the first test revealed a small amount of metal shavings from the MMLS test apparatus which were visually separated from the detached material samples. The metal shavings were from metal components of

MMLS that contacted during use. Physical separation of the detached pavement particles and metal shavings was required to prevent inflation of the detached particulate resultant mass. Separation was done using tweezers and a magnet to remove asphalt particulate which was magnetic. It should be noted that asphalt pavement can become magnetic if foundry sand, a ferrous byproduct of steel forming, is used in the pavement aggregated (USDOT 2016).Separated pavement material and metal shaving from the second 48 hour cure time coal-tar-based test are shown below in Figure 2-1. Once separated the particulate was transferred into their respective vial which were then stored at room temperature for up to two weeks until the particulate was prepared for GC/MS analysis, as discussed in Section 4.5.

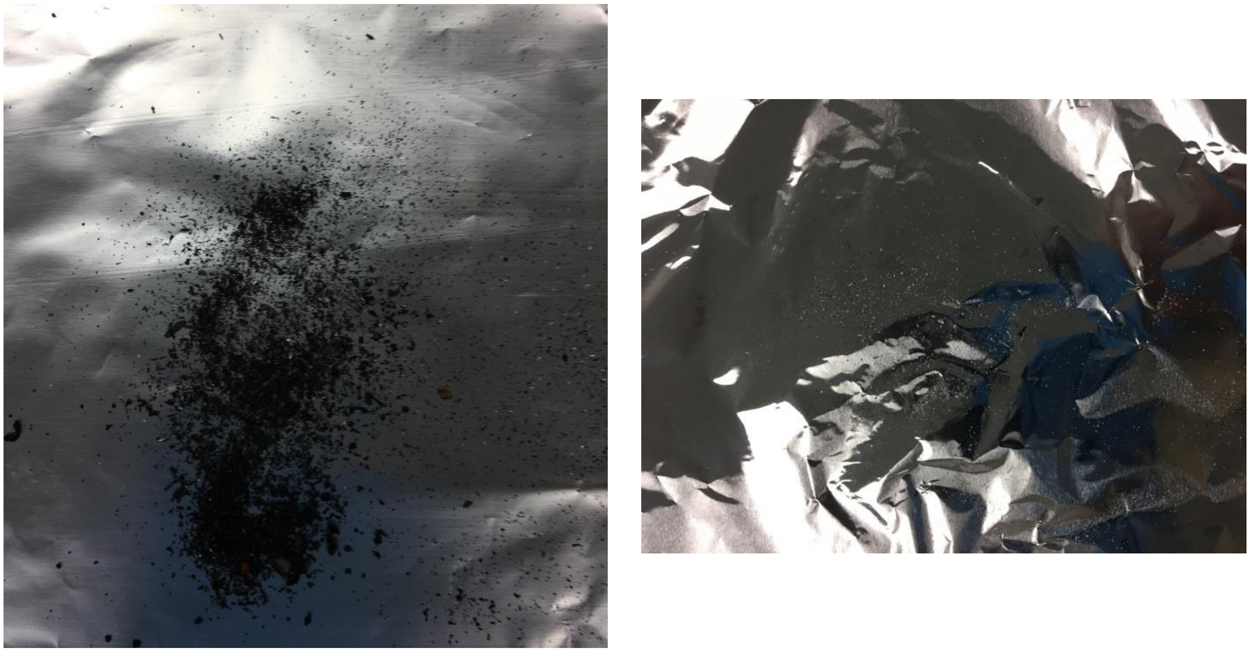

Figure 4-3: Detached Pavement (Left) and Metal Shaving (Right) After Separation

4.3 Sample Disc Material Selection and Preparation

As discussed in Section 2.3 the intended purpose of a pavement rejuvenation product is to replenish oxidized oil resins in the asphalt pavement binder. All tests performed used aged asphalt that had evident signs of oxidation such that rejuvenation product application would be more prototypical with respect to rejuvenation of a new asphalt sample. In order for pavement samples to be installed into the MMLS clamping mechanism’s unique geometric pavement configuration, which is shown in Figure 4-2, modification to the core samples was required. Pavement sample discs had a six inch diameter and an overall thickness of 4 inches. Two parallel edges were cut four inches apart on each disc. Based on these prescribed disc dimensions the top surface area of each discs was 22.08 in^2, as calculated in Appendix B.

Test discs were cut from six inch diameter core samples drilled on two separate days from asphalt pavement located at an industrial site located in Western Massachusetts. The site owner identified four separate pavement sections that were available to extract cores. Prior to the final site selection a visual assessment of the physical conditions of each site was performed. Site investigation considered visual oxidation, crack formations, surface contamination, and asphalt age relative to the other potential site.

The final site selected, shown below in Figure 4-4, was a section of access road with asphalt estimated to be 20 years old, based on discussion with property owner. In addition the owner indicated that the road had limited use in the past five years decreasing the likelihood of surface contamination, which could lead to irregularities in baseline organic compound loading, from vehicular traffic. This particular section of asphalt had no signs of snow removal unlike the majority of the complex, which further suggested limited use. It should be noted that snow was removed with a metal shovel on the first day cores were extracted prior to beginning.

Figure 4-4: Asphalt Prior to Core Extractions on 2/26/2019 (Left) and 3/28/2019 (Right)

Cores were cut on February 26th, 2019 and March 28th, 2019. All core samples were cut in close proximity to one another using a KOR-IT® electric core drill with a continuous cooling water feed into the attached six inch diameter coring bit. As discussed by Peterson 1984, and summarized above in Section 2.3, asphalt is complex mixture of chemical compounds which vary widely from mix to mix. To ensure asphalt cores were from the same original asphalt batch, and thus have a similar baseline PAH compound concentration prior to product application, a tight sampling location of approximately fifteen feet long by ten feet wide was implemented. Extracted cores and their respective core holes are shown below in Figure 4-5 and Figure 4-6, from 2/26/2019 and 3/28/2019, respectively. In total 50 cores were taken on the 26th and 66 cores were taken on the 28th. It should be noted that core depths varied by location.

Figure 4-5: Asphalt Cores from 2/26/ 2019 (Left) and Respective Asphalt Core Holes (Right)

Figure 4-6: Asphalt Cores from 3/28/ 2019 (Left) and All Asphalt Core Holes (Right)

In the lab asphalt cores were cut to the proper disc dimensions as prescribed previously. Discs were originally cut using a Diamond Laser 7000 Diamond Band Saw, however a MK Diamond tile saw was ultimately used to improve cut quality. Cut discs were washed and lightly scrubbed with a soft bristled scrub brush and warm town water to remove residual left from the cutting processes. Discs were allowed to completely dry for a minimum of 24 hours prior to rejuvenation product application.

Rejuvenator application was volumetrically controlled on a per disc basis such that application rates were uniform for all tests. The rejuvenator application rate used was 0.08 gallons of rejuvenator per square yard of pavement treated for consistency with the application rate used by Barr et al. 2018 so test results could be directly compared to the results previously obtained by Barr et al. 2018. This target application was confirmed to be within the range of acceptable application rates recommended by each product manufacture.

The rejuvenator application rate was converted to 5.16 mL per disc (see Appendix B). The volume of rejuvenator was measured out with a 2 to 10mL ranged automatic pipette made by Finnpipette® with a new pipette tip attached for each set of discs prepared. The coal-tar-based and the bio-based products were pipetted as is, directly from the containers they were received. The asphalt-based product required a 1:1 dilution with water prior to application. Therefore 30 mL of the asphalt-based product was combined and mixed with 30 mL of regular tap water in a glass beaker prior to pipetting. Regardless of product type, once measured with the automatic pipette the product was ejected onto the intended disc. A rubber spatula was used to spread the rejuvenator until a uniformly distributed coat was achieved on the disc surface. It should be noted that prior to the first use, the automatic pipette was gravimetrically verified by extracting a predetermined volume of water and then discharging the water into a pre-weighed beaker. The beaker was weighed again and the mass of water was converted to a volume based on density to confirm correct pipette function. After a set of discs were coated the automatic pipette tip was discarded and the spatula was thoroughly cleaned.

4.4 Sand Abrasion Test Procedure

Sand, typical to that used during snow/ice events, was applied to pavement samples discs prior to tire contact with the MMLS to evaluate the influence of sand on rejuvenated surfaces degradation and PAH compound transport. Six tire abrasion tests were performed with sand having characteristics typical of sand used during a winter storm placed on the test discs prior to the operation of the MMLS test apparatus. The six tests followed the procedure established in Section 4.2, with additions of the preparation and application of winter storm sand prior to a test case start and the separation of applied sand from the detached material prior to quantification. For the six tests, which are outlined in Table 4-4, two tests were performed coal-tar-based, bio-based, and asphalt-based rejuvenators, respectively.

Sand placed on sample discs was selected to have physical characteristics, specifically bulk density and grain size distribution, that satisfied typical industry winter storm sand standards and recommendations, as provided in Section 2.4. Winter storm sand was obtained from a local municipality stockpile. A grain size distribution via sieve analysis was completed for the entire lot of sand that would be used for tests, as described below in Section 4.4.1, to confirm acceptable characteristics. Sand was pre-weighed prior to each test in a manner such that uniform gradation and consistent application from test to test was achieved, as discussed in Section 4.4.2. Once prepared sand was evenly applied to the discs and the test was run. At test completion all detached material and winter storm sand was collected in the same manner as discussed above in Section 4.2. Sand was then separated from the detached asphalt surface material as discussed in Section 4.4.3 before the final mass of detached material was determined.

4.4.1 Sand Sieve Analysis

A grain size distribution of the sand selected for uses was preformed to ensure the characteristics of the sand selected were similar to that of sand typically required by municipalities and state highway departments for use during a winter storm event. The quantity of sand used for the grain size distribution was distributed into two pre-weighed pans, weighed, and placed into an over at 105°C to dry prior to starting the grain size distribution. The sand was left in the oven for one hour and both trays were then reweighed. If the weight was not within 0.1 grams of the original weight the tray was placed back in the oven and was allowed 20 more minutes of dry time. After 20 minutes each tray was re-weighed and compared to the previous weight. This process was repeated until two consecutive weights taken 20 minutes apart were within 0.1 grams of each other as shown in Table 4-2.

Table 4-2: Sand Drying Prior to Grain Size Distribution

Time	12:50 PM	1:00 PM	2:00 PM	2:20 PM	2:40 PM
Tray ID	**Mass of Tray [g]**	**Mass of Tray +Sand [g]**	**Mass of Tray +Sand [g]**	**Mass of Tray +Sand [g]**	**Mass of Tray +Sand [g]**
Tray 1	36.3	641.9	629.5	629.2	629.3
Tray 2	36.1	615.6	604.4	604.2	604.1

Once confirmed dry a grain size distribution analysis was performed with the dried sand using a Gilson Sieve Shaker and the following USA Standard Test Sieve sizes; 3/8", No. 4, No. 8, No. 50, No. 100, and No. 200. Each sieve and bottom the pan were verified clean and weighed prior to instillation into the sieve shaker. Sieves were installed sequentially increasing in screen open size from the bottom up as shown in Figure 4-7 below. Dry sand was placed in the top sieve, the sieve shaker lid was secured, and the shaker was run for a total of 15 minutes.

Figure 4-7: Sieve Shaker Setup (Left) and Samples from Each Sieve Size (Right)

After fifteen minutes each sieve was removed and a final weight for each sieve was obtained. The final results of the grain size distribution in terms of percent of mass retained and percent of mass passing each sieve size are provided in Table 4-3. After each sieve was weighed the contents were emptied into individual containers based on grain size for use in the preparation of sand samples for each test. Figure 4-7 above shows a sample of each grain size retained by sieve size, with left most beaker containing material retained on the No. 4 screen and the right most beaker containing material that passed through to the pan.

Table 4-3: Winter Storm Sand Size Distribution

Sieve Size	Percent Retained [%]	Percent Passing [%]
3/8”	0%	0.0%
No. 4	6.3%	6.3%
No. 8	20.5%	26.8%
No. 50	59.2%	86.0%
No. 100	10.7%	96.6%
No. 200	1.9%	98.5%
Pan	1.5%	100%

4.4.2 Sand Preparation

The quantity of sand applied to each set of discs was determined on a mass per unit area rate based on the application rates provided in Section 2.4. To increase the magnitude of particulate detachment from a single sand application, based on the hypothesis established in Section 3.0, the maximum recommended application rate of 375 pounds per lane mile was used. The application rate was converted to 2.68 grams of sand per square foot, assuming a 12 foot wide travel lane. The total per test application rate for coverage over six discs was calculated to be 2.47 grams by multiplying the nominal surface area of single disc as established in Section 4.3, the application rate, and the total number of discs installed per test.

To improve consistency from test to test individual grain sizes were proportionally weighed out based on the gradation results above. To allow for separation of detached material, which was magnetic as discussed in Section 4.2, each gain size was passed with a magnet prior to weighing sand for a test to remove any potentially magnetic grains. The mass of each grain sized used for a given test is provided below in Table 4-4. Weighed sand was then uniformly spread out on the surface test discs.

Table 4-4: Per Test Mass of Individual Sand Grain Sizes

Sieve Opening Size	Mass of Grain Size per Test [g]
3/8”	0.000
No. 4	0.156
No. 8	0.506
No. 50	1.461
No. 100	0.263
No. 200	0.046
Pan	0.037
Total Mass	2.470

4.4.3 Detached Material - Sand Separation

At the completion of a given test run collected detached material contained sand particles from the executed test. To separate sand from the detached pavement material, all collected contents were spread out on a clean sheet of aluminum foil. Tweezers were used to separate larger particles and a magnet was used to separate out the smaller particles. Multiple passes with the magnet were made until an acceptable separation was achieved as shown below Figure 4-8 for the second sand abrasion test run with coal tar coated samples. It should be noted that black particles seen in the glass beaker containing the sand are predominately abraded rubber from the tires of the MMLS test apparatus.

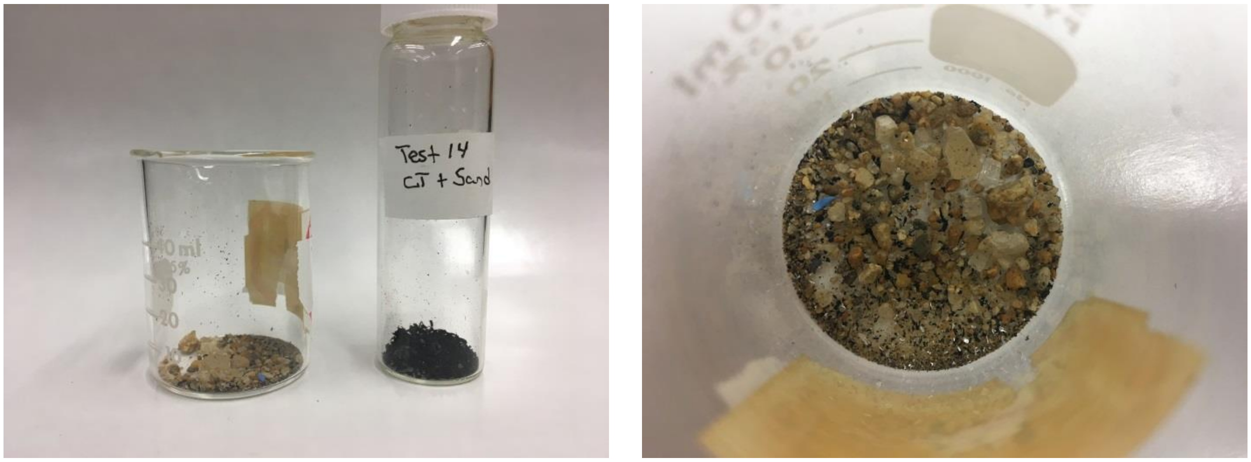

Figure 4-8: Detached Material – Sand Completed Separation

4.5 GC/MS Processing

Prior to Gas Chromatography/Mass Spectrometry (GC/MS) analysis, analytes of interest were extracted from the detached particulate samples with methylene chloride and spiked with an internal standard as discussed below in Section 4.5.1. Additionally external standards were prepared at four different concentrations (discussed in Section 4.5.2) and used during all GC/MS sequences.

GC/MS analysis was completed with an Agilent Technologies (Santa Clara, CA) 7890B GC system with a 5977A MSD. The system had an HP-5ms ultra inert 30 m x 250 µm x 0.25 µm column, suitable for analysis with semi-volatile compounds, installed. The length of the column used was previously calibrated and verified to a length of 31.99 mm. Helium was the GC carrier gas used at a flow rate of 1 mL/min and a pressure of 7.8 psi. The initial GC oven temperature was 40°C and was held for four minutes. A ramp rate of 10°C per minute was then used until an oven temperature of 290°C was achieved. The final oven temperature was held for 15 minutes prior to sequence completion. The thermal aux transfer line to the MS was set at 200°C. The sequence time for a single vial was 44 minutes.

Sample vials were run in two sequences. The first sequence contained four test sample vials, one from each product type plus the control, along with the five external standards. This short sequence was completed to ensure adequate sample dilution such that analyte concentrations fell within the detection limits of the system without detector saturation and within the prepared external standard concentrations such that data extrapolation would not be required. Adequate sample dilution was confirmed and a sequence with the remaining sample vials, well as five additional external standards, was completed.

After sequence completion, GS/MS results were analyzed with the MS ChemStation –G1034C software package and Excel. Chromatographs, which are provided in Appendix D for each external standard and detached pavement sample processed, were integrated with the auto-integration software function. The integrated area and the associated average retention time for each peak were exported to Excel. Analytes of interested were first identified for each external standard by peak matching based on the molecular weight of each analytes (see Table 2-3) and the expected order compounds would elute (USDOI 2006). Analytes were identified in the external standard with the highest analyte concentration first to increase separation between analyte peaks and background peaks (particularly important for the lowest concentration standard). This was repeated for all four concentrations of the external standards prepared and established the anticipated analyte retention times. All analyte peaks were individually checked with the MS result against the NIST mass spectral library contained in the ChemStation software for further confirmation.

Analytes in each sample were determined via peak matching based on the retention times established with the external calibration. Peaks were manually checked with the MS. Retention times for analytes in samples that did not elute were manually checked. If low concentration peaks existed but were not captured by the auto-integration function, the peaks were manually integrated in the software package and the integrated areas were included.

Peak area data for analytes of interested identified in a given sample was converted to the respective analyte concentrations based on the known reference standard concentrations. Linear interpolation for a particular analyte concentration was used based on the integrated analyte area, and the two closest integrated areas and concentrations of the respective analyte standard. These results are presented in Section 5.2.

4.5.1 PAH Extraction and Sample Preparation for GC/MS Processing

Analytes of interest required extraction from detached particulate material prior to GC/MS analysis. Solvent based extraction was performed with high purity mobile phase for HPLC and/or extraction solvent for GC applications methylene chloride with a purity greater than 99.9%.. The same methylene chloride was used for all aspects of extraction (including glassware cleaning) and was purchased from Fisher Scientific (Waltham, AM).

For a given test detached particulate was transferred from its respective storage vial into a 200 mL volumetric flask cleaned as described in Section 4.6. Particulate that remained in the vial were flushed to the volumetric flask with methylene chloride. In some cases multiple flushes were required for complete particulate transfer. The remainder of the volumetric flask was filled to the 200 mL gradation line with methylene chloride. This is shown below in Figure 4-9 for the detached material/methylene chloride solution prepared from the first asphalt-based sand abrasion test.

Figure 4-9: Methylene Chloride Solution Prepared for Sonication

Contents in the flask were swirled multiple times to suspend all particles within the flask. The flask was placed in a sonication bath for a minimum of ten minutes to facilitate analyte extraction. After the sonication bath the contents in the flask were transferred into a clean beaker to allow a small volume of each sample to be filtered prior to GC/MS analysis. Solution samples were filtered through AHLSTROM 0.45 Micron PTFE membrane filters attached to a BD 5 ml syringe with a Luer-Lok® tip. The PTFE membrane filter was selected because PTFE is resistant to aggressive solvents such as methylene chloride. Filtered solutions were transferred directly into clean vials with minimal headspace for future transfer into GC/MS glass vials. Remaining unfiltered solution was transferred into clean amber bottles for storage. All samples were stored at 4°C prior to use.

A single internal standard was used for GC/MS analysis to verify consistent GC/MS operation for all samples process. Perylene-d12 had an expected retention time near the average retention time of analytes of interest and was not expected to co-elute with peaks of interest (USDOI 2006) and was selected as the internal standard. A 1 mL certified reference standard of perylene-d12 dissolved in methylene chloride at a concentration of 1000 µg/mL was purchased from FisherScientific® and diluted to a concentration of 100 µg/mL for internal standard use.

For GC/MS analysis 1.3 mL of each previously filtered test sample was measured with a 2 mL glass pipette and transferred into a 1.5 mL GC/MS vial that had been twice rinsed with methylene chloride. Ten microliters of the 100 µg/mL per was then injected into the sample using a ten microliter syringe for a final perylene-d12 concentration of 0.76 µg/mL.

4.5.2 External GC/MS Standards

Three certified 1 mL reference standards manufactured by SPEX CertiPrep™ were purchased from FisherScientific® to prepare external GC/MS calibration standards for each analyte evaluated, as listed above in Table 2-3. The three standards contained 16 individual PAH compounds, carbazole, and acridine at concentrations of 2000 µg/mL methylene chloride, 1000 µg/mL methylene chloride, and 1000 µg/mL methanol, respectively. A five step series of dilutions, reducing each standard concentration by a factor of ten, was performed with methylene chloride, for each reference standard to generate the respective external standards. It should be noted that methylene chloride was used to dilute the acridine as the original methanol solvent would be reduced by a factor of 1000 prior to the first use as a reference standard at a concentration of 1 ppm acridine.

The series of dilution was completed to the following general procedure. All pipettes, glass vials, and GC/MS vials were rinsed twice with new methylene chloride and allowed to air dry before use. Each reference standard was opened and transferred into a unique labeled glass vial with a screw top lid. With a clean pipette, 9 mL of new methylene chloride was injected into each glass vial. Vial lids were secured and each vial was inverted multiple times to mix the solution. To reduce the total number of GC/MS vials required, the PAH and carbazole external standards were combined during the next stage of the serial dilution. Acridine was not included in this mixture as to not introduce methanol. Thus, 1 mL of previously prepared 16 PAH solution, at a concentration of 200 ppm, and 1 mL of the previously prepared carbazole solution, at a concentration 100 ppm, were combined with 8 mL of new methylene chloride in a clean labeled vial. Similarly, 1 mL of the previously prepared acridine solution at a concentration of 100 pm was combined with 9 mL of new methylene chloride in a separate vial. Each time a solution was transferred a new clean pipette was used. The process was repeated a total of five times. The final prepared solutions and their respective concentrations are shown Table 4-5 below. It should be noted that merged columns in the table below indicate solutions with combined reference standards. Figure 4-10 below shows each vial of prepared PAH external standard solution in decreasing concentration from left to right.

Table 4-5: External Standard Series of Dilutions

<table>
<tr><th>Dilution #</th><th>16 PAH Solution Concentration</th><th>Carbazole Concentration</th><th>Acridine Concentration</th></tr>
<tr><td>1</td><td>200 ppm</td><td>100 ppm</td><td>100 ppm</td></tr>
<tr><td>2</td><td colspan="2">20 ppm / 10 ppm</td><td>10 ppm</td></tr>
<tr><td>3</td><td colspan="2">2 ppm / 1 ppm</td><td>1 ppm</td></tr>
<tr><td>4</td><td colspan="3">0.2 ppm / 0.1 ppm / 0.1ppm</td></tr>
<tr><td>5</td><td colspan="3">0.02 ppm / 0.01 ppm / 0.01 ppm</td></tr>
</table>

Figure 4-10: Prepared PAH Solution Standards

Prepared external standards were then transferred from preparation vials into clean 1.5 mL GC/MS vials for analysis. GC/MS external standard vials were not prepared for standards at concentrations at or greater than 100 ppm as this could saturate the GC/MS detector. All external standard solution that was not transferred to GC/MS vials was refrigerated in their respective vials at 4°C in case additional standards were required.

4.6 Glassware Cleaning Procedure

Clean glassware reduces the potential of cross-contamination of solution samples prepared for GC/MS analysis. Prior to use, glassware was rinsed with warm tap water and thoroughly cleaned with Citrinox® acid detergent, diluted with water to an approximate concentration 2% detergent by volume. Glassware was filled with Citrinox® solution and allowed to soak. Glassware was rinsed multiple times in warm tap water until visually free from detergent. Regent grade water made from a Thermo Scientific 7150 water purification system was then used to rinse each piece of glassware. All glassware was rinsed at minimum twice with the reagent grade water. Glassware to be used for the solvent extraction described in Section 4.6 was oven dried at 105°C for a minimum of 4 hours. Other glassware, such as vials for particulate storage were allowed to air dry at room temperature overnight prior to final cleansing.

Once dry all glassware was twice rinsed with methylene chloride to remove any remaining organic compounds. Glassware was filled with enough methylene chloride, approximately 20 percent of the maximum gradation mark, to allow the methylene chloride to be swirled around all surfaces of the glassware. This process was repeated twice for each piece of glassware. Methylene chloride used for the second rinse of any glassware could be used to perform the first rinse of another glassware item. However all secondary methylene chloride rinses were done with fresh, unused methylene chloride. Glass pipettes and vials used for GC/MS analysis were only twice rinsed with reagent grade water and methylene chloride, and not cleaned with soap and water prior to use.

5.0 Results and Analysis

As discussed above in Section 4.1, a total of 19 tests were performed to evaluate pavement particulate detachment and associated PAH contaminate concentration as the result of pavement surface challenges. The results in terms of detached particulate and contaminate release are presented in Section 5.1 and Section 5.2, respectively.

5.1 MMLS Test Results - Detached Particulate

Cumulative potential solid phase PAH compound and aromatic heterocyclic hydrocarbon compound transport is dependent on the mass of material detached and the respective compound concentrations in the detached material, from a defined pavement surface area. It is therefore insufficient to make an assessment of the contaminate mobilization potential based on the mass of detached material alone. Specifically, if the detached particulate mass from pavement treated with a coal-tar-based rejuvenator is significantly less than a control (untreated asphalt), for example, but the compound concentration in the coal-tar-based particulate is much higher than the control, the cumulative contaminate release of the coal-tar-based product could be more severe. Therefore this discussion is reserved for the chemical analysis discussion below.

Particulate detachment is a metric which can be used to assess performance of the coal-tar-based, asphalt-based, and bio-based rejuvenator products. Results from the 19 simulated pavement surface abrasion tests in terms of detached particulate material are presented in Table 5-1 and Figure 5-1 below. The plot in Figure 2-1Figure 5-1 presents the results for each parameter evaluated in terms of the minimum, maximum, and average mass of detached particulate. Data series are labeled with "AS", "Bio", and "CT" for asphalt-based, bio-based, and coal-tar-based rejuvenator products, respectively. This nomenclature, which is used for all plots in the present section, is then preceded by "48 Hr", "3 Wks", and "Sand", for abrasions tests completed after a 48 hour cure time, a three week cure time, and after the application of sand, respectively. With the exception of the three tests that evaluated particulate detachment from pavement treated with a coal-tar-based rejuvenator after a 48 hour cure time, all conditions evaluated only had duplicate tests run. Therefore, for each parameter shown the minimum and maximum values provided in Figure 5-1, represent the two measured values and the average value is the average of two data points. For comparison purposes the three measured data points for the coal-tar-based tests that had a 48 hour cure time are shown as the minimum, maximum, and average value.

As such the average value shown on the plot is the third data point measured and not the true statistical average.

Table 5-1: Detached Material per Test

Product Type	Cure Time/Run #	Sand Application [Y/N]	Detached Material Mass [g]	Product Type	Cure Time/Run #	Sand Application [Y/N]	Detached Material Mass [g]
Control	N/A	N	3.2097	Asphalt	48 Hr. Run 2	N	0.3136
Control	N/A	N	1.9238	Asphalt	48 Hr. Run 1	Y	0.7267
Coal-Tar	48 Hr. Run 1	N	0.6922	Asphalt	48 Hr. Run 2	Y	2.1737
Coal-Tar	48 Hr. Run 2	N	0.2932	Bio-Base	48 Hr. Run 1	N	5.3721
Coal-Tar	48 Hr. Run 3	N	0.454	Bio-Base	48 Hr. Run 2	N	4.3442
Coal-Tar	3 Week Run 1	N	0.8817	Bio-Base	3 Week Run 1	N	2.5006
Coal-Tar	3 Week Run 2	N	0.870	Bio-Base	3 Week Run 2	N	2.6991
Coal-Tar	48 Hr. Run 1	Y	0.6193	Bio-Base	48 Hr. Run 1	Y	4.2851
Coal-Tar	48 Hr. Run 2	Y	0.6059	Bio-Base	48 Hr. Run 2	Y	3.2126
Asphalt	48 Hr. Run 1	N	0.3795				

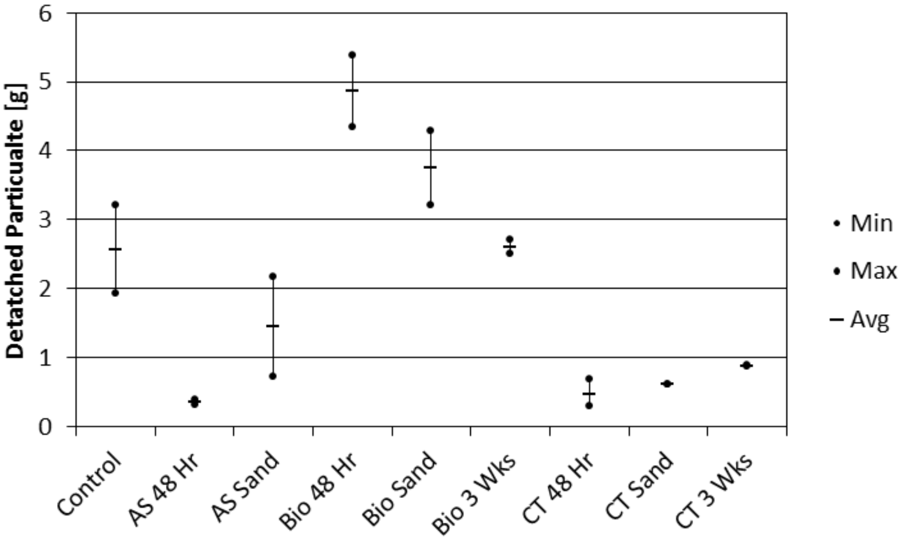

Figure 5-1: Detached Material per Test

As seen above, overall rejuvenator performance based on particulate detachment differed by rejuvenator type, rejuvenator cure time, and after a single sand application. Rejuvenator performance relative to particulate detachment following a 48 hour cure time on a product by product basis is of interest. A 48 hour cure time before vehicular traffic resumes following rejuvenator application is a common industry standard and therefore is the most probable to occur. The average mass of particulate detachment from samples treated with asphalt-based and coal-tar-based rejuvenators proceeding a 48 hour cure time were 0.347 g and 0.480 g, respectively. This mass of detached material was lower than that from the control which had an average detached material mass of 2.567 g, or the test samples treated with the bio-based product which had the highest average detached material mass of 4.858 g. Two notable differences between pavement samples treated with the bio-based rejuvenator and the coal-tar and asphalt based rejuvenators was visual surface roughness and apparent rejuvenator cure after 48 hours.

With respect to surface roughness a visual difference could be seen between the bio-based rejuvenator and the coal-tar and asphalt based rejuvenators. Specifically, the viscous nature of both the coal-tar and asphalt-based rejuvenators resulted in partial infill of surface imperfections which subsequently hardened whereas the bio-based rejuvenator slowly absorbed into the pavement. The smoother surface finish of the asphalt-based and coal-tar-based products likely contributed to the lower respective detached particulate quantities than the control or bio-based tests.

A 46.5% decrease in average detached particulate (4.858 g to 2.599 g) was observed for samples treated with the bio-based rejuvenator followed by a three week cure time with respect to a 48 hour cure time. It was noted that samples treated with the bio-based rejuvenator were damp to the touch following the 48 hour cure time whereas after a three week cure time similar samples had a drier surface finish. This suggests that after 48 hours the bio-base rejuvenator had not effectively cured and possibly weakened surface particle bonds with the bulk pavement structure at that time, based on the higher average particulate detachment. Conversely, the average mass of detached particulate from samples treated with the coal-tar-based rejuvenator increased by 82.6% (0.4798 g to 0.8759 g), when the rejuvenator application was followed by three weeks. This is shown in Figure 5-2 below which presents the average mass of detached pavement material 48 hours and three weeks after a rejuvenator application. It should be noted that quantities of material detached from samples treated with the asphalt-based rejuvenator were excluded as only 48 hour cure time test were completed.

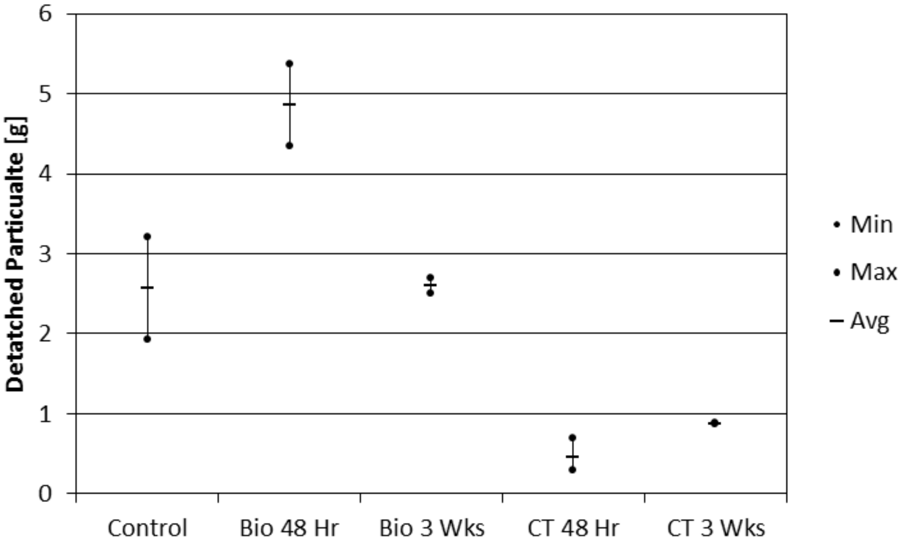

Figure 5-2: Rejuvenator Cure Time Effects on Detached Particulate Mass

As seen in Figure 5-2, the variation of measured detached particulate quantities was small for rejuvenated samples that had a three week cure time relative samples that had 48 hour cure time. The percent difference between the two measured detached particulate quantities from pavement treated with the bio-based and coal-tar-based rejuvenators after a 48 hour cure time was 21.2% and 81.0%, respectively. After a three week cure time the percent difference were lower for samples treated with the bio-based and coal-tar-based rejuvenators, 7.6% and 1.3% respectively. Reduction in variation between measured data points with respect to cure time suggest the application of a rejuvenator, once a sufficient cure time has been achieved, will result in a more homogenous surface structure was with respect to resiliency to surface challenges. Additional triplicate data points for all test cases are required to confirm this.

Pavement samples were treated with rejuvenation products, followed by a 48 hour cure period prior to the application of sand and simulated tire contact. With respect to samples that had the same rejuvenators applied and allowed the same 48 hour cure time but did not have sand applied, the rate of particulate detachment increased for samples treated with the coal-tar-based and asphalt-based rejuvenators. Particulate detachment decreased for pavement samples treated with the bio-based rejuvenator. This is highlighted below in Figure 5-3.

An observed increase in particulate detachment as a result of sand application was anticipated for all test cases as hypothesized in Section 3.0. This was not the case for samples treated with the bio-based rejuvenator. As mentioned above, the bio-based rejuvenator was damp to the touch after 48 hours. At the completion of both bio-based test runs that included a sand application, sand particles were observed embedded in the rejuvenated pavement surface, a possible cause for the reduced particulate detachment.

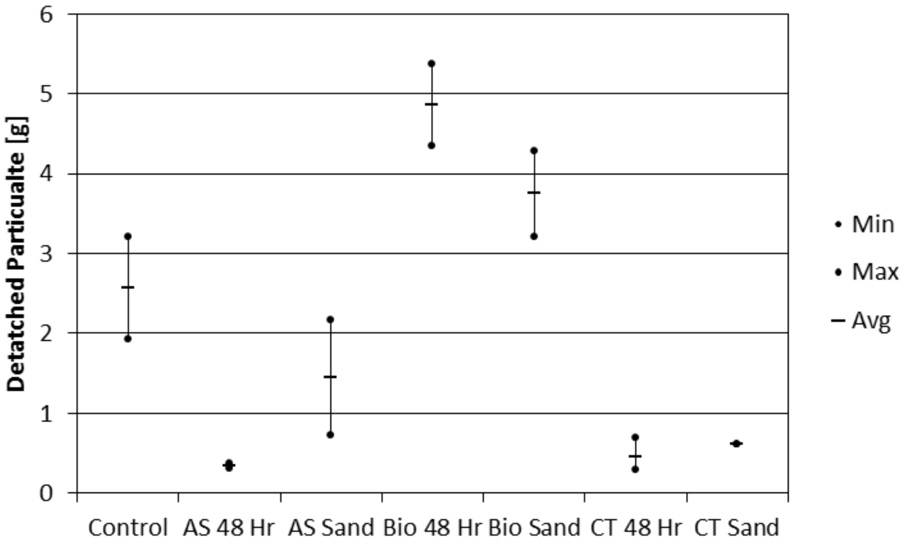

Figure 5-3: Sand Application Effects on Rejuvenated Pavement Particulate Detachment

5.2 Chemical Analysis Results

All detached pavement material was chemically analyzed via gas chromatography/mass spectrometry to quantify 16 PAH compounds and two aromatic heterocyclic hydrocarbon compounds present in the detached material. The chemical quantification results for each analyte of interest detected in samples of detached rejuvenated pavement are present in Table 5-2 below in terms of milligram of analyte per kilogram of pavement material analyzed. These results are leveraged and manipulated throughout the present section to make an assessment of potential solid phase contaminate loading as a result of rejuvenated pavement surface material detachment. This analysis is done primarily with the 16 PAH compounds identified below. Discussion related to aromatic heterocyclic hydrocarbons, particularly carbazole and acridine, follow.

Table 5-2: Analyte Concentration per Mass of Detached Particulate by Test

Analyte	Control Run 1	Control Run 2	Coal-Tar-Based 48 Hour Cure Run 1	Coal-Tar-Based 48 Hour Cure Run 2	Coal-Tar-Based 48 Hour Cure Run 3	Coal-Tar-Based 3 Week Cure Run 1	Coal-Tar-Based 3 Week Cure Run 2	Coal-Tar-Based 48 Hour Cure Sand, Run 1	Coal-Tar-Based 48 Hour Cure Sand, Run 2	Bio-Based 48 Hour Cure Run 1	Bio-Based 48 Hour Cure Run 2	Bio-Based 3 Week Cure Run 1	Bio-Based 3 Week Cure Run 2	Bio-Based 48 Hour Cure, Sand, Run 1	Bio-Based 48 Hour Cure, Sand, Run 2	Asphalt Based 48 Hour Cure Run 1	Asphalt Based 48 Hour Cure Run 2	Asphalt-Based 48 Hour Cure, Sand, Run 1	Asphalt-Based 48 Hour Cure, Sand, Run 2
Naphthalene	-	-	29.2	-	-	22.8	-	16.5	39.5	-	-	-	-	-	4.0	-	-	-	-
Acenaphthylene	-	-	-	-	-	8.0	-	-	-	-	-	-	-	-	-	-	-	-	-
Acenaphtene	2.5	-	92.1	30.4	29.3	64.2	29.6	52.6	102.9	-	-	-	-	-	-	14.8	-	-	-
Fluorene	-	2.8	148.3	47.2	63.0	102.3	55.1	91.8	172.5	-	-	-	-	2.7	3.3	-	-	-	-
Phenanthrene	3.2	37.2	895.1	290.9	347.1	610.9	282.1	436.7	1118.1	2.0	3.9	25.3	24.3	20.8	26.1	61.2	-	20.5	3.9
Anthracene	-	10.0	207.3	93.9	127.2	159.1	83.0	148.7	259.2	-	-	7.0	5.2	5.5	7.4	-	-	-	-
Acridine*	-	-	40.3	-	-	43.0	23.8	38.9	64.2	-	-	-	-	-	-	-	-	-	-
Carbazole*	-	17.5	135.8	95.1	105.8	131.8	91.0	108.1	211.3	-	-	13.8	15.6	7.9	12.2	-	-	-	-
Fluoranthene	3.1	40.0	495.1	261.1	309.3	431.4	266.7	365.4	729.5	1.8	-	2.5	36.8	20.6	30.1	89.6	-	26.7	6.6
Pyrene	11.0	42.9	356.6	211.8	245.1	335.7	213.4	282.2	529.2	7.2	12.4	31.5	36.1	28.3	34.2	88.3	18.5	33.6	8.1
Benz(a)anthracene	-	58.3	273.0	216.6	213.4	281.5	203.8	266.2	461.3	2.3	8.5	39.1	44.5	24.6	29.0	89.8	-	20.3	5.0
Chrysene	-	45.2	275.9	236.9	254.3	306.3	224.4	317.5	478.1	-	14.4	49.9	51.6	31.1	35.0	155.8	-	31.3	9.8
Benzo(b)fluoranthene	-	111.5	239.2	293.4	269.6	299.8	242.1	283.0	467.7	7.0	19.0	59.9	58.5	42.5	40.1	199.9	-	36.2	-
Benzo(k)fluoranthene	-	77.9	278.9	304.8	262.8	345.3	239.7	297.8	565.1	-	-	65.0	80.1	28.8	40.6	-	-	-	-
Benzo(a)pyrene	-	143.5	297.5	354.2	318.8	343.2	290.4	350.9	562.8	-	11.4	67.8	69.5	38.2	45.5	232.8	-	27.8	5.0
Indeno(1,2,3-c,d)pyrene	-	21.2	176.8	-	134.2	197.2	159.1	176.7	395.3	-	-	-	22.8	23.3	14.9	-	-	-	-
Dibenz(a,h)anthracene	-	-	64.6	57.9	38.4	68.6	56.2	56.1	154.5	-	-	-	4.0	-	-	-	-	-	-
Benzo(g,h,i)perylene	-	33.9	135.1	104.8	107.6	159.2	126.2	136.2	358.5	-	5.6	28.5	21.2	18.9	17.3	65.6	-	-	-

Notes:

1) All concentrations are provided in units of mg analyte per kg detached material
2) * Indicates aromatic heterocyclic hydrocarbon compounds
3) – indicates concentrations below the detection limits of the GC/MS

The cumulative concentration of the 16 PAH compounds quantified per mass of detached material was calculated in units of milligrams 16PAHs measured per kilogram of detached particulate, which will be expressed as mgΣ16PAH/kg in all text, tables, and figures in the present section. The cumulative concentration for each test was calculated by summation of all compounds quantified for a given test above in Table 5-2, excluding acridine and carbazole. The calculated cumulative PAH compound concentrations are provided in Table 5-3.

Table 5-3: Cumulative PAHs per Mass of Detached Material

Test Condition	Coal-Tar-Based [mg Σ16PAH/kg]	Bio-Based [mg Σ16PAH/kg]	Asphalt-Based [mgΣ16PAH/kg]
48 Hour Cure Time Run 1	3964.6	20.2	997.7
48 Hour Cure Time Run 2	2720.0	75.2	18.5
48 Hour Cure Time Run 3	2503.9	-	-
48 Hour Cure Time Run 1 - Sand	3278.5	285.4	196.5
48 Hour Cure Time Run 2 - Sand	6394.1	327.6	38.4
3 Week Cure Time Run 1	3735.5	376.6 ± 166.3	-
3 Week Cure Time Run 2	2720.0	454.6	-
Control Run 1 [mg Σ16PAH/kg]		19.8	
Control Run 2 [mg Σ16PAH/kg]		624.4	

The calculated cumulative PAHs per mass of detached particulate are plotted below on a test by test basis Figure 5-4 below. This plot, and all subsequent plots in this section are configured the same as in Section 5.1. As seen in the figure below particulate from pavement treated with the coal-tar-based rejuvenators had a cumulative PAH compound concentration a full order of magnitude higher than that measured in all control, asphalt-based, and bio-based test cases. This confirms the hypothesis stated above in Section 3.0, which was based on previous research conducted with coal-tar-based sealants which have a lower coal tar contents.

The variation in cumulative PAH compound concentration per mass of detached particulate is larger for particulate detached from pavement treated with the coal-tar-based rejuvenator with respect to detached particulates from pavement treated with the bio-based and asphalt based rejuvenators. Given the relatively low mass particulate of particulate analyzed, less than one gram per sample, and the relatively high PAH concentration in the coal-tar-based rejuvenator with respect to asphalt-based and bio-based rejuvenator, the relative effect on the cumulative PAH concentration per mass of detached particulate from a few inert pavement particles or particles with only a partial rejuvenator coating can be significant.

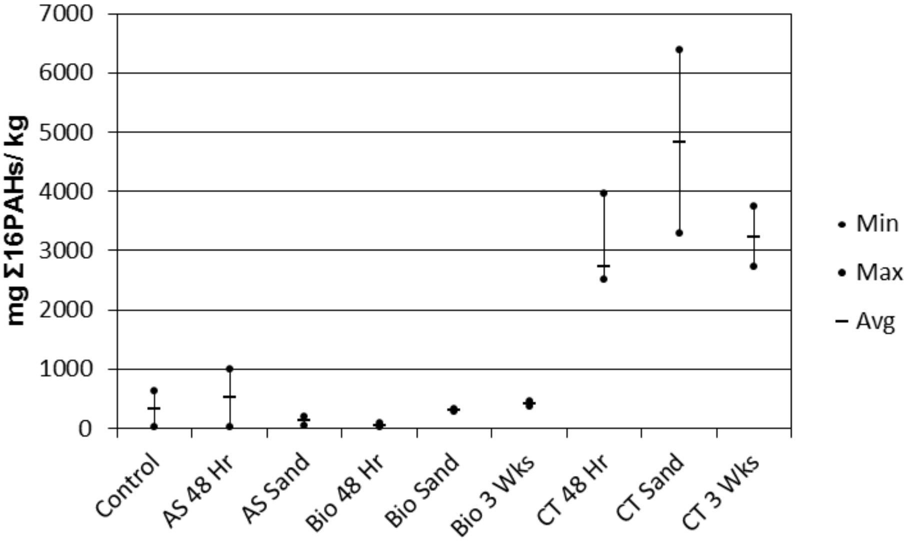

Figure 5-4: Cumulative PAHs per Mass of Detached Material

As seen in Figure 5-5 below, the cumulative concentration of PAH compounds in material detached from pavement treated with the bio-based rejuvenator varied with product cure time when sand was not applied. The average concentration of PAH compounds in particulate detached from samples treated with the bio-based rejuvenator and subjected to tire abrasion after 48 hours was 47.7 mg16PAHs/kg which was less than the average concentration of 415.6 mg16PAH/kg measured in samples that had a 3 week cure time. The increase in PAH compound concentration with time may be attributed to the bio-based rejuvenator extracting PAH compounds from deeper in the asphalt material to the surface where particulate detachment occurs, although further research is required to affirm.

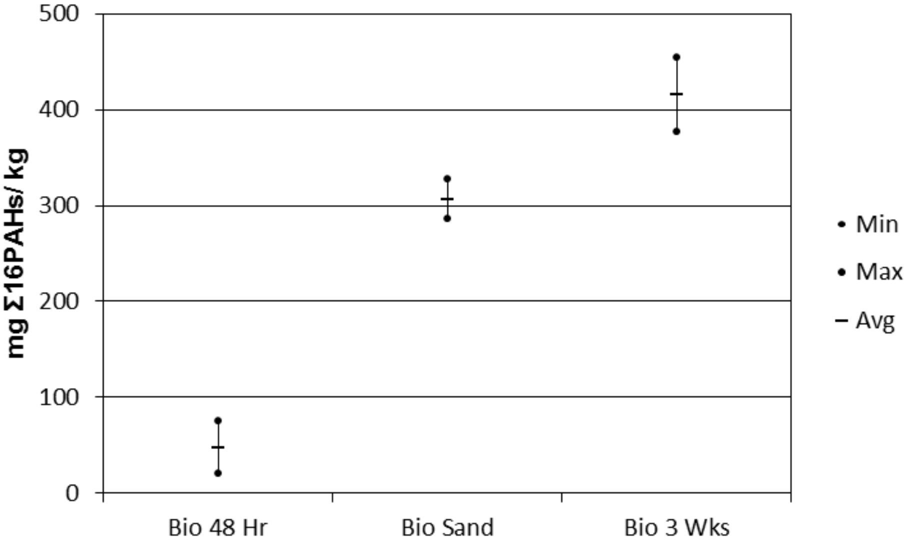

Figure 5-5: Total PAH Loading in Detached Material Treated with Bio-Based Rejuvenator

The most valuable parameter used to assess the potential for environmental contamination with respect to solid phase PAH compound transport form the use of pavement rejuvenation products is the measured concentration of PAH compounds in detached particulate normalized by the surface area that the particulates were detached from. This was done by multiplying the cumulative concentration of the 16 PAH compounds present in Table 5-3, by their respective mass of detached material (presented in Table 5-1), and then dividing by the total surface area of the sample discs (0.92 ft^2 as determined in Appendix B). The normalized result, in terms of milligram of the 16 PAH compounds analyzed per area of pavement rejuvenated, is provide in Table 5-4. Not included in the table are the normalized PAH loadings for the two control tests which were 0.1 and 1.3 mg16PAH/ft^2 of pavement rejuvenated. Also included in the table below is the average normalized PAH concentration for all test performed with each rejuvenator.

Table 5-4: Cumulative PAH Concentration Normalized by Pavement Surface Area

Test Condition	Coal-Tar-Based [mg 16PAH/ft^2]	Bio-Based [mg 16PAH/ft^2]	Asphalt-Based [mg 16PAH/ft^2]
48 Hour Cure Time Run 1	2.98	0.12	0.41
48 Hour Cure Time Run 2	0.80	0.35	0.01
48 Hour Cure Time Run 3	1.34	-	-
48 Hour Cure Time Run 1 – Sand	2.21	1.33	0.16
48 Hour Cure Time Run 2 – Sand	4.21	1.14	0.09
3 Week Cure Time Run 1	3.58	1.02	-
3 Week Cure Time Run 2	1.34	1.33	-
Average of Normalized Concentration	2.35	0.88	0.17

Normalization of the measured PAH concentrations by the surface area particulate was detached from accounts for both the concentration of PAH compounds contained in a given mass of particulate as well as the mass of particulate detached from a given area of pavement. Based on the tables above, although the bio-based product had a much higher detachment rate than the coal-tar-based rejuvenator but the overall PAH compound contamination potential is lower for the bio-based compared to the coal-tar-based rejuvenator because the PAH compound concentration was much higher in coal-tar-based rejuvenator. Based on the test cases evaluated and the average normalized PAH concentrations for all products above the following assessment can be made; with respect to the cumulative PAH compound loading per unit area the coal-tar-based rejuvenator had the largest potential for PAH contamination, followed by the bio-based and then the asphalt based. To affirm these results additional tests with the asphalt-based rejuvenator with a three week cure time should be done, at a minimum.

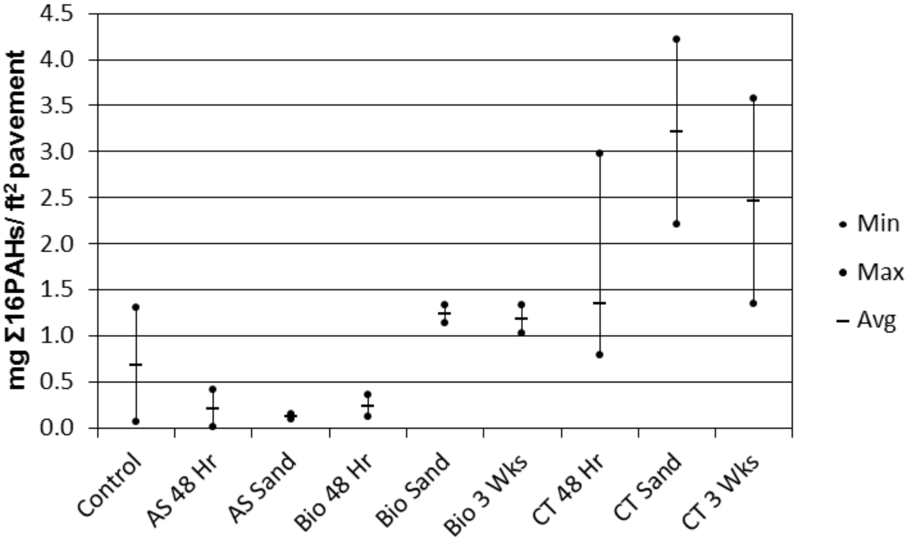

Figure 5-6: Cumulative PAH Compound Loading per Unit Area of Pavement

The individual compounds released are also of interest in addition to cumulative values presented above. Figure 5-7 below provides a breakdown of the product type average individual compound concentrations per mass of detached material analyzed in samples where particulate detachment occurred 48 hours after product application. Individual compounds are arranged by increasing molecular weight form naphthalene to benzo(g,h,i)perylene. As seen for the particulate samples detached pavement treated with a coal-tar-based sealer, the most prominent compound detected was phenanthrene followed by fluoranthene and benzo(a)pyrene

In addition to the 16 PAH compounds quantified acridine and carbazole, two aromatic heterocyclic compounds, were also quantified. As seen in the raw test data above as well as the figure below, acridine was only detected in samples that contained pavement particles treated with the coal-tar-based rejuvenator. Concentrations of acridine detected were low and represented a small fraction of the cumulative contaminate concentration quantified in samples. The measured concentration of acridine when above the detection limit ranged from 23.8 to 64.2 mg/kg solid sample. Carbazole was identified in all samples that contained pavement treated with the coal-tar-based rejuvenators at concentrations that exceeded that of acridine. Measured carbazole concentrations in those particular samples ranged from 91.0 to 211.3 mg/kg solid sample. Carbazole also was detached in one control sample and four bio-based samples; all at concentrations lower than 20 mg/kg solid sample.

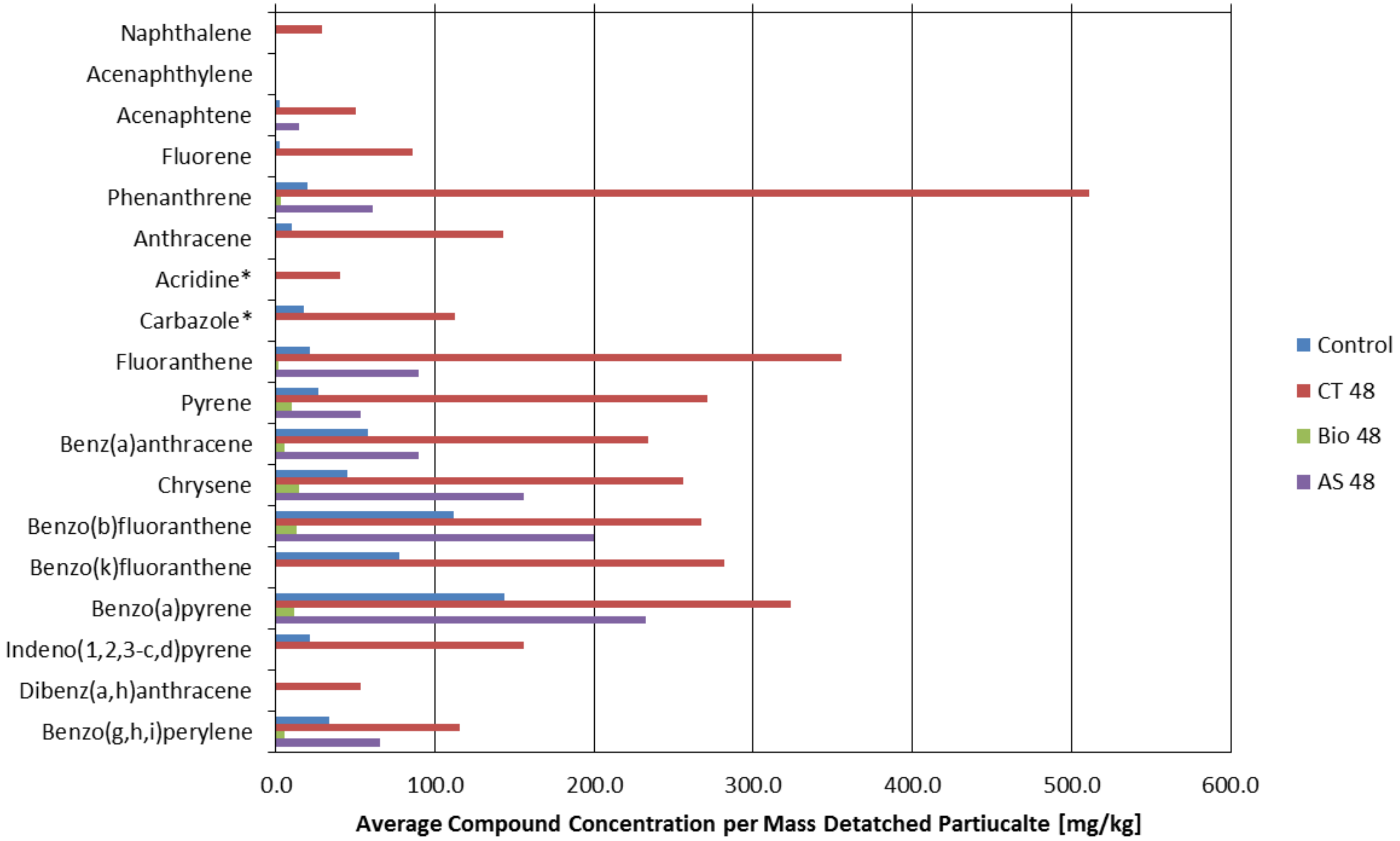

Figure 5-7: Average Individual Compound Concentrations per Mass of Detached Material for 48 Hour Cure Time Tests

6.0 Conclusion

Research was conducted with a model mobile load simulator to replicate pavement surfaces challenges resultant from rolling tire contact on pavement treated with three rejuvenator products types (coal-tar-based, asphalt-based, and bio-based) to quantify the contamination potential form solid-phase transport of 16 PAH compounds contained in detached surface material. In total 19 pavement surface abrasion test were performed to evaluate the influence of rejuvenator cure time, evaluated at 48 hours and three weeks after product application, and a single sand application (typical of slippery road conditions from snow and ice) on surface particle detachment and subsequent PAH compound loading.

With respect to particulate detachment, pavement samples treated with the coal-tar-based and asphalt-based rejuvenators had improved performance 48 hours after application (average detachment of 0.480 g and 0.347 g, respectively) compared to the control (not treated) and bio-based rejuvenators (average detachment of 2.567 g and 4.858 g respectively). However, despite a lower surface particulate detachment rate, the average cumulative concentration of the 16 PAH compounds measured normalized by the rejuvenated pavement sample area for the same 48 hour coal-tar cure time was 3.21 $mg\Sigma16PAH/ft^2$ of pavement rejuvenated, which was higher than the bio-based, asphalt-based, and control samples, 0.24, 0.21, and 0.69 $mg\Sigma16PAH/ft^2$, respectively. Furthermore, for all conditions evaluated the concentration of PAH compounds measured per mass of detached particulate was at a minimum an order of magnitude higher in samples from pavement treated with a coal-tar-based rejuvenator.

7.0 References

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Appendix A Coal Tar Pavement Preservation Products

The following appendix contains Table A-1 and Table A-2 which presents the mass fraction of coal tar or coal tar pitch and the trade-name coal tar based rejuvenation and sealcoat products, respectively. All data present here was obtained from the technical data sheets and/or the material safety data sheets of the respective products. This data was used in previous sections for comparison of coal tar content between seal coat and rejuvenation products.

Table A-1: Coal Tar Content of Tradename Rejuvenators

Company/Manufacture Name	Product Tradename	Percent Coal-Tar by Mass
RejuvaSeal®	RejuvaSeal®	35% to 50% ASTM D490 RT 12 Coal Tar
Hydro-Labs, Inc.	CPR™	40% to 52% ASTM D490 RT 12 Coal Tar
Asphalt Technology Restoration System Inc.	Pavement Dressing Conditioner (PDC)	< Refined Coal Tar
Garden State Sealing	P-629 Coal Tar Sealer/Rejuvenator	35% to 50% ASTM D490 RT 12 Coal Tar 14% to 40% Coal-Tar Oils

Table A-2: Coal Tar Content of Tradename Sealcoats

Company/Manufacture Name	Product Tradename	Percent Coal-Tar by Mass
SealMaster®	Coal Tar Ultra Blend Sealer	20% to 40% Coal Tar Pitches
GemSeeal® Pavement Products	GemSeal® Pro-Blend	10% to 30% Coal-Tar Pitch
Neyra®	Tarconite Coal Tar Pavement Sealer	25% to 35% Coal Tar
STAR, Inc.	Star Seal – Asphalt Pavement Sealer Star-Seal Supreme, Premium Grade Pavement Sealer	29% to 32% Coal Tar Pitch

Appendix B Supplemental Asphalt Discs Preparation Information

This appendix contains the following supplemental information related to the collection and preparation of asphalt discs prior to instillation in the MMLS; a calculation used to determine the surface area of each asphalt disc and a brief rejuvenator application rate calculation

Asphalt Disc Surface Area Calculation

The surface area calculation shown below is based on Figure B-1, which is a schematic of the asphalt disc geometry. In the figure below, the shape of the asphalt disc is shown in black and all reference marks are made in blue.

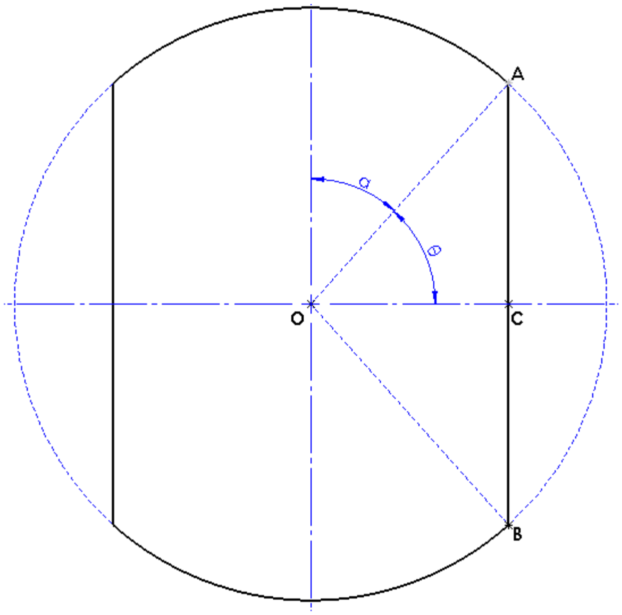

Figure B-1: Schematic of Asphalt Disc

Define Known Lengths:

- Line AO = BO = radius of the disc = 3 inches
- Line CO = ½ the distance between the two parallel faces = 2 inches

Length of line AC Based on Triangle ACO

$$AC^2 + CO^2 = AO^2$$

$$AC = \sqrt{AO^2 - CO^2} = \sqrt{3in^2 - 2in^2} = 2.24in$$

Area of Triangle ABO

$$A_{\Delta ABO} = \frac{1}{2}bh$$

$$A_{\Delta ABO} = \frac{1}{2}(AB)(CO) = \frac{1}{2}(2.24in * 2)(2in) = 4.47in^2$$

Area of Arc α

$$Sin(\theta) = \frac{CB}{BO} = \frac{2.24in}{3in}$$

$$\theta = 48.19°$$

So,

$$2\alpha + 2\theta = 180$$

$$2\alpha = 180° - 2(48.19°) = 83.62°$$

Then,

$$A_{arc} = \frac{1}{2}\pi r^2 \frac{2\alpha}{180}$$

$$A_{arc} = \frac{1}{2}\pi(3in^2)\left(\frac{86.32°}{180°}\right) = 6.57in^2$$

Total Disc Surface Area

$$A_{disc} = 2A_{Arc} + 2A_{\Delta ABO}$$

$$A_{disc} = 2(6.57in^2) + 2(4.47in^2) = 22.08in^2$$

Rejuvenator Application Rate Determination

The following brief calculation was done to convert the rejuvenator application rate of 0.08 gal rejuvenator/yard^2 asphalt established in Section 4.3 to the required amount of rejuvenation product to be applied to each asphalt disc.

$$0.08\frac{gal}{yard^2} * 3785.4\frac{ml}{gal} * 0.00077\frac{yard^2}{in^2} = 0.23\frac{ml}{in^2}$$

$$0.23\frac{ml}{in^2} * 22.08\frac{in^2}{Disc} = 5.16\frac{mL}{disc}$$

Appendix C Abrasion Test Photos

The following appendix contains photographs taken from each test performed with the MMLS test apparatus. There are 19 total pages in this appendix, one for each test performed. Tests are organized by rejuvenator type in the following order with the exact test conditions outlined in the caption; control, coal-tar-based, bio-based, and asphalt-based. For each test there is a photo of the discs prior to product application, immediately after product application, the discs installed in the MMLS prior to and after a test run, detached particulate in the aluminum foil immediately after the installed discs, and detached material past aluminum foil liner. It should be noted that the photos of the discs before and after product application were not applicable to the control tests.

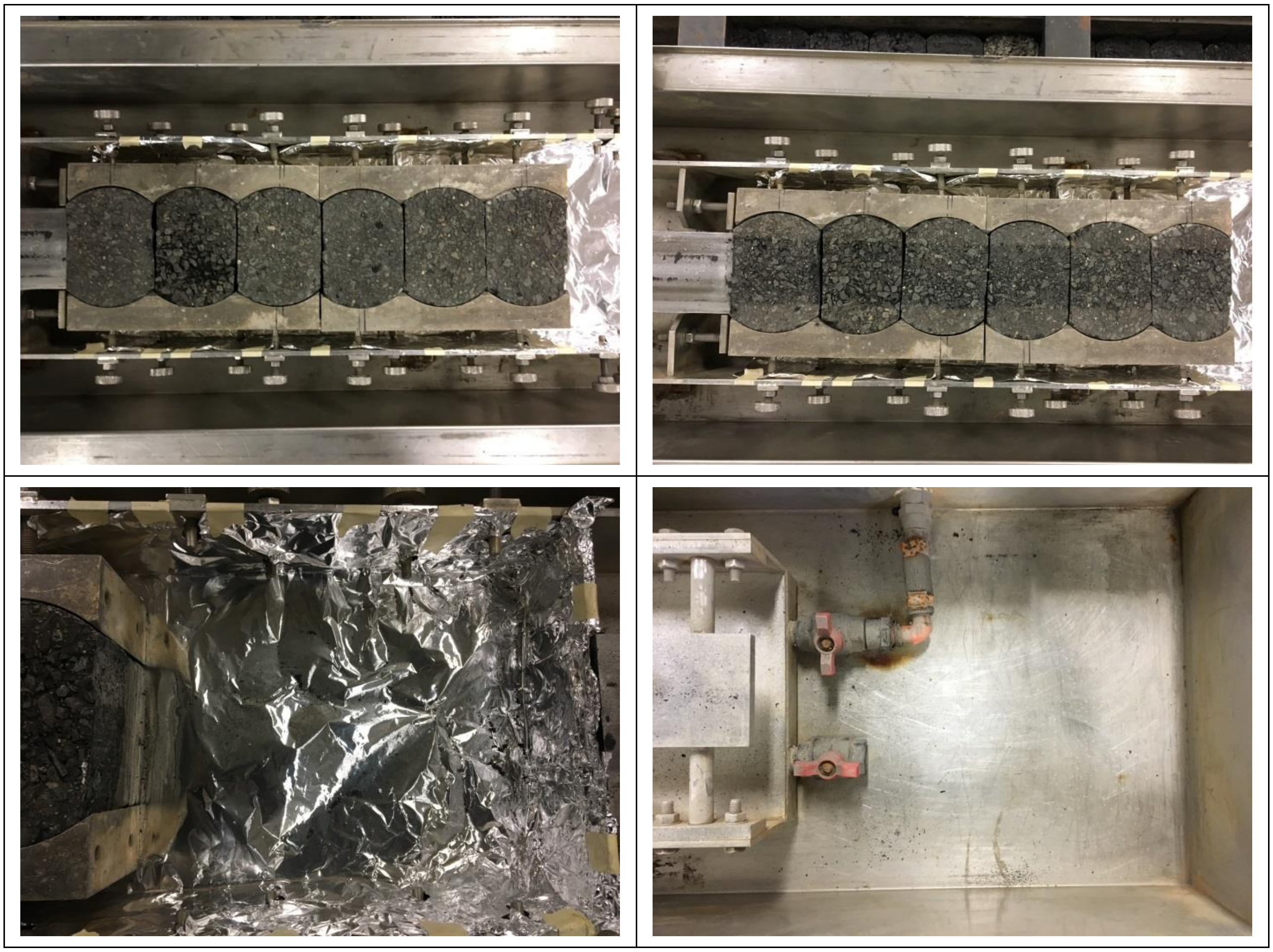

Figure C-1: Control Test #1

Figure C-2: Control Test #2

Figure C-3: Coal-Tar-Based, 48 Hours Cure Time, Test #1

Figure C-4: Coal-Tar-Based, 48 Hour Cure Time, Test #2

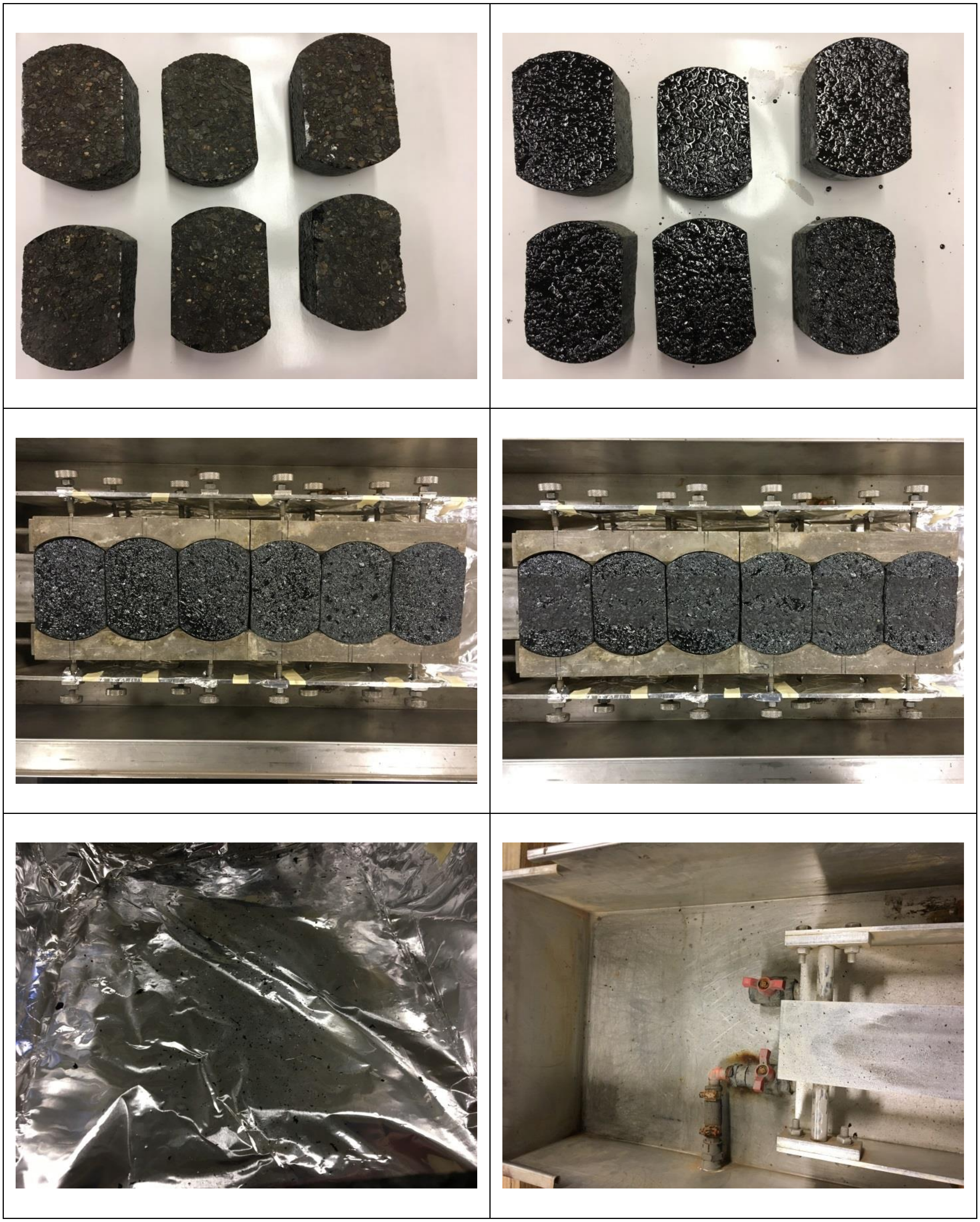

Figure C-5: Coal-Tar-Based, 48 Hour Cure Time, Test #3

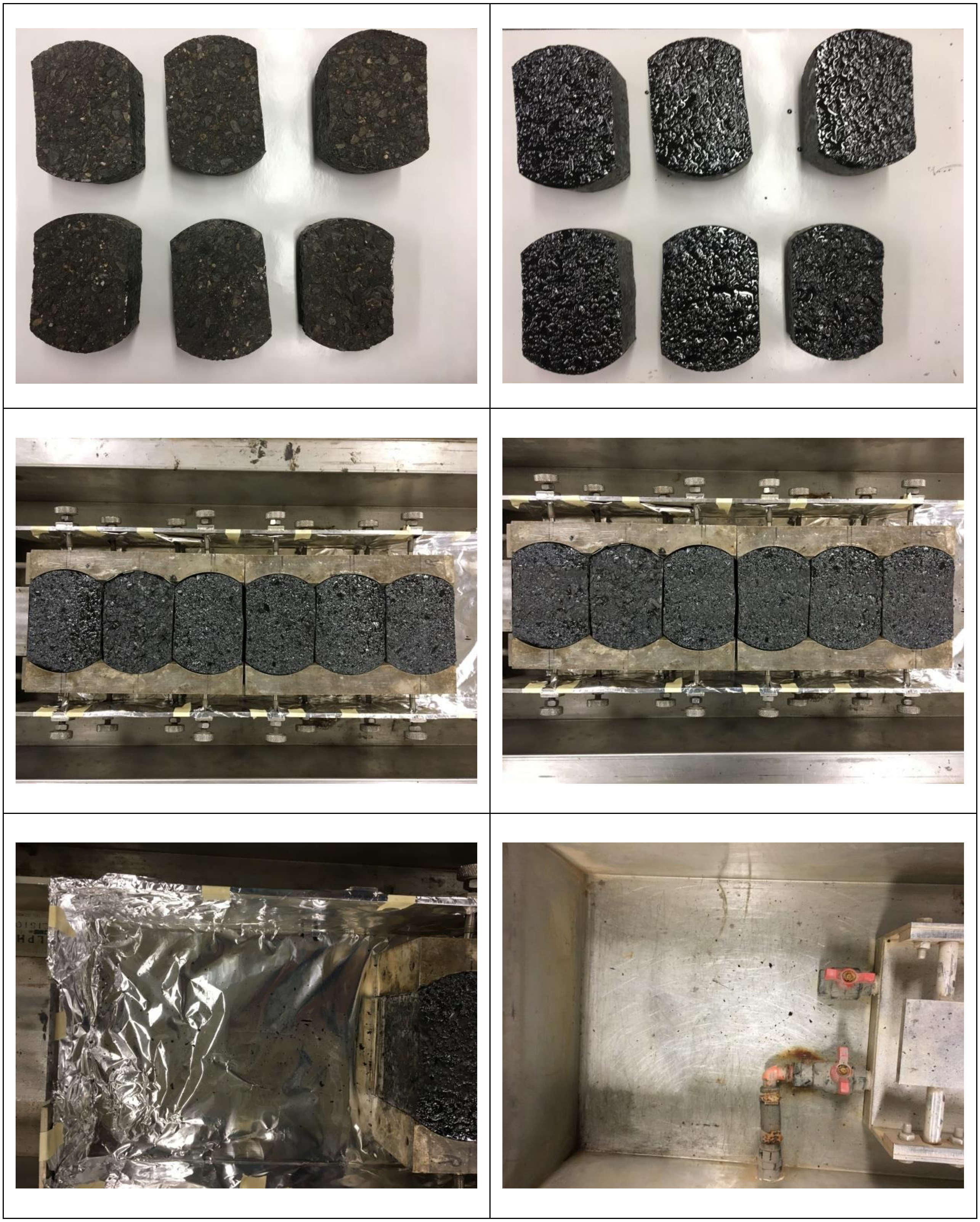

Figure C-6: Coal-Tar-Based, 3 Week Cure Time, Test #1

Figure C-7: Coal-Tar-Based, Three Week Cure Time, Test #2

Figure C-8: Coal-Tar-Based, 48 Hour Cure Time, Sand Application, Test #1

Figure C-9: Coal-Tar-Based, 48 Hour Cure Time, Sand Application, Test #2

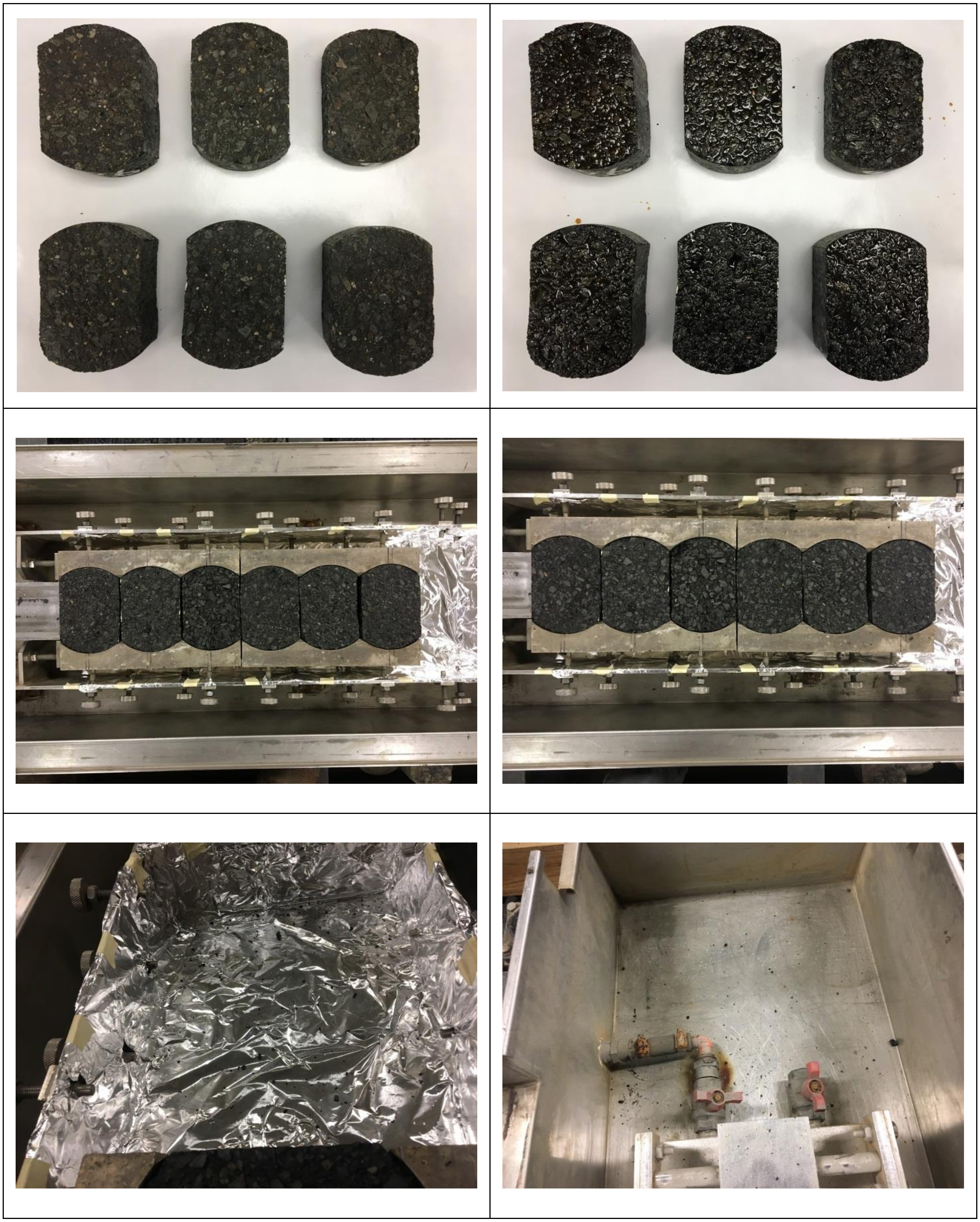

Figure C-10: Bio-Based 48 Hour Test #1

Figure C-11: Bio-Based, 48 Hour Cure Time, Test #2

Figure C-12: Bio-Based, 3 Week Cure Time, Test #1

Figure C-13: Bio-Based, 3 Week Cure Time Test #2

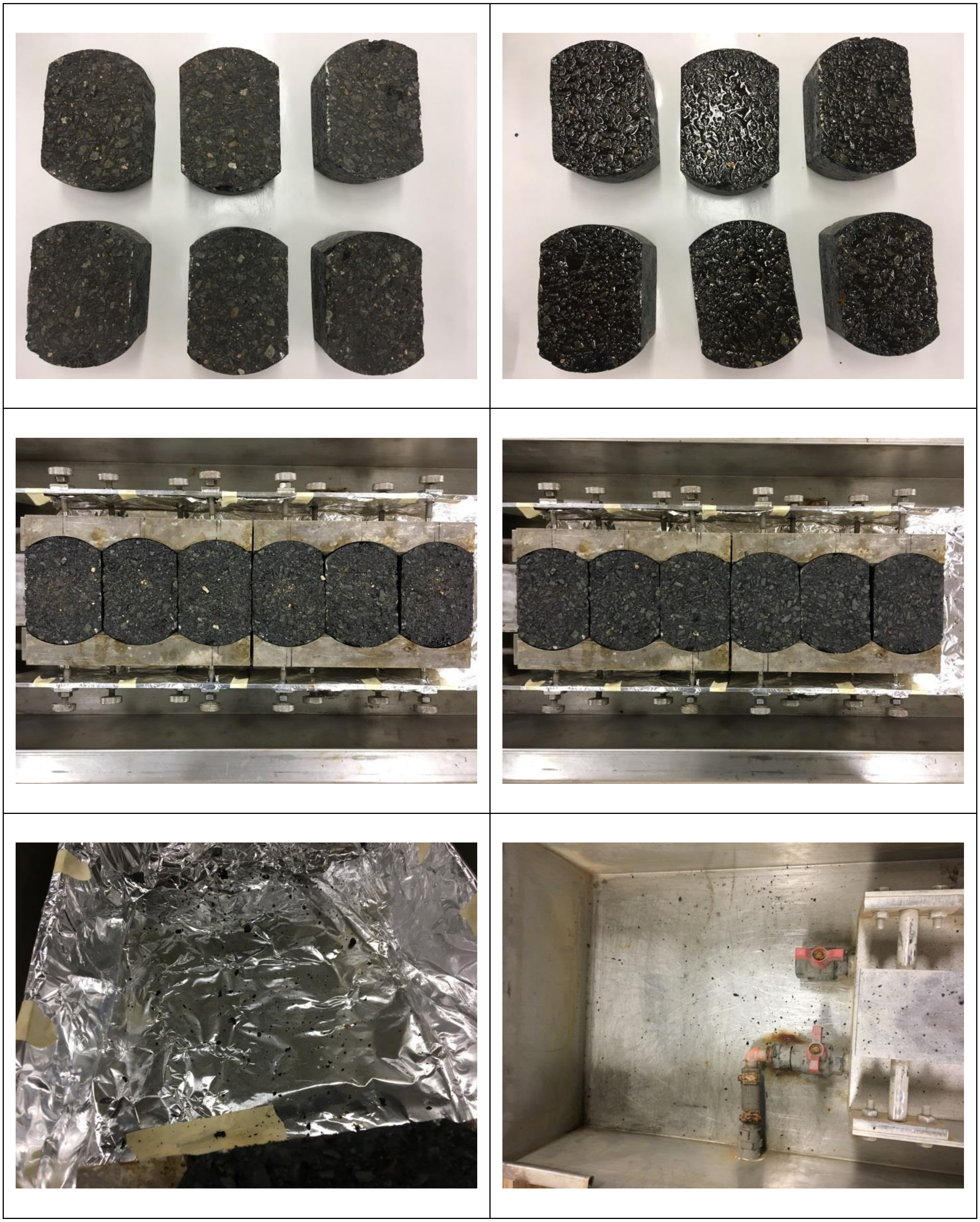

Figure C-14: Bio-Based, 48 Hour Cure Time, Sand Application, Test #1

Figure C-15: Bio-Based, 48 Hour Cure Time, Sand Application, Test #2

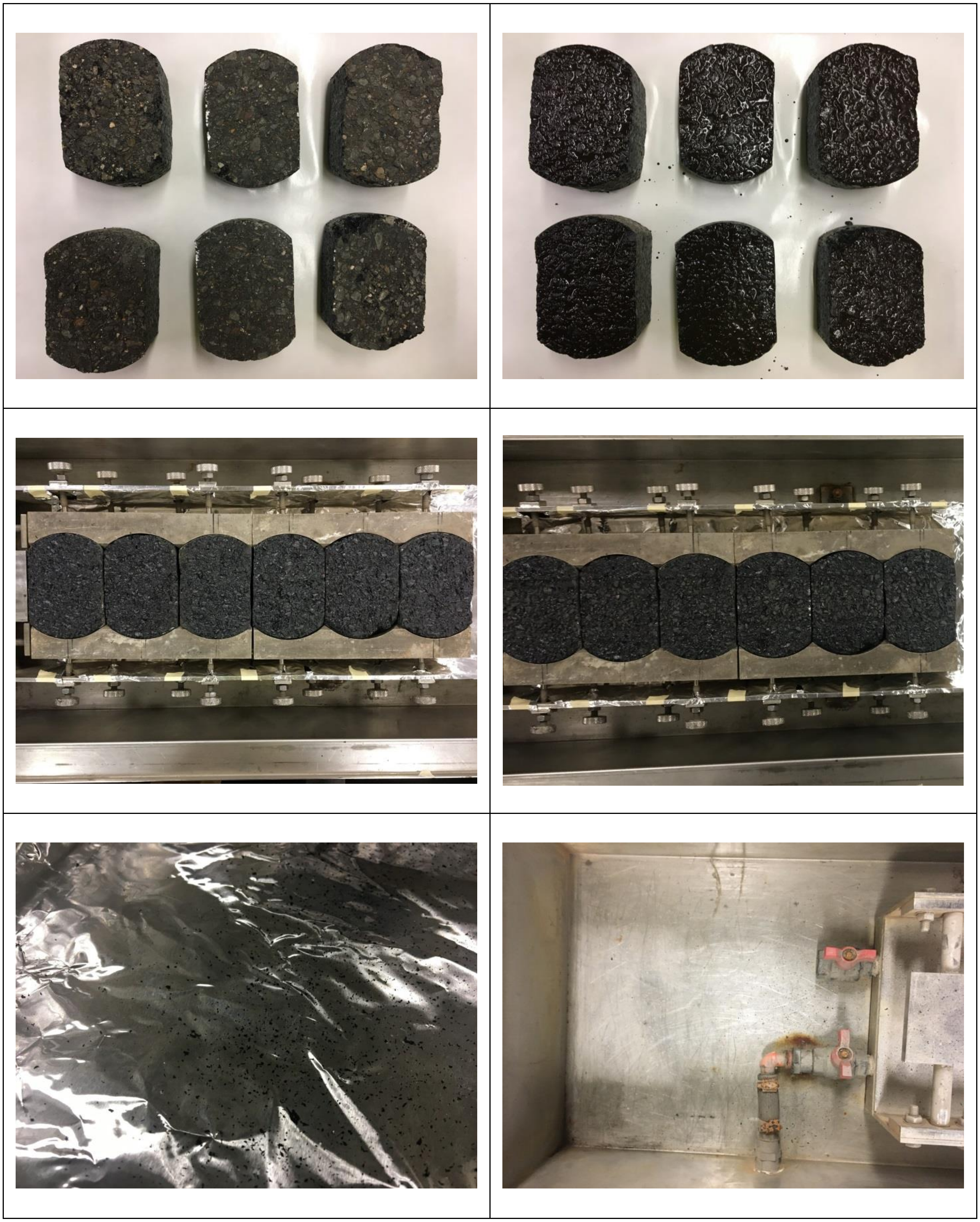

Figure C-16: Asphalt-Based, 48 Hour Cure Time, Test #1

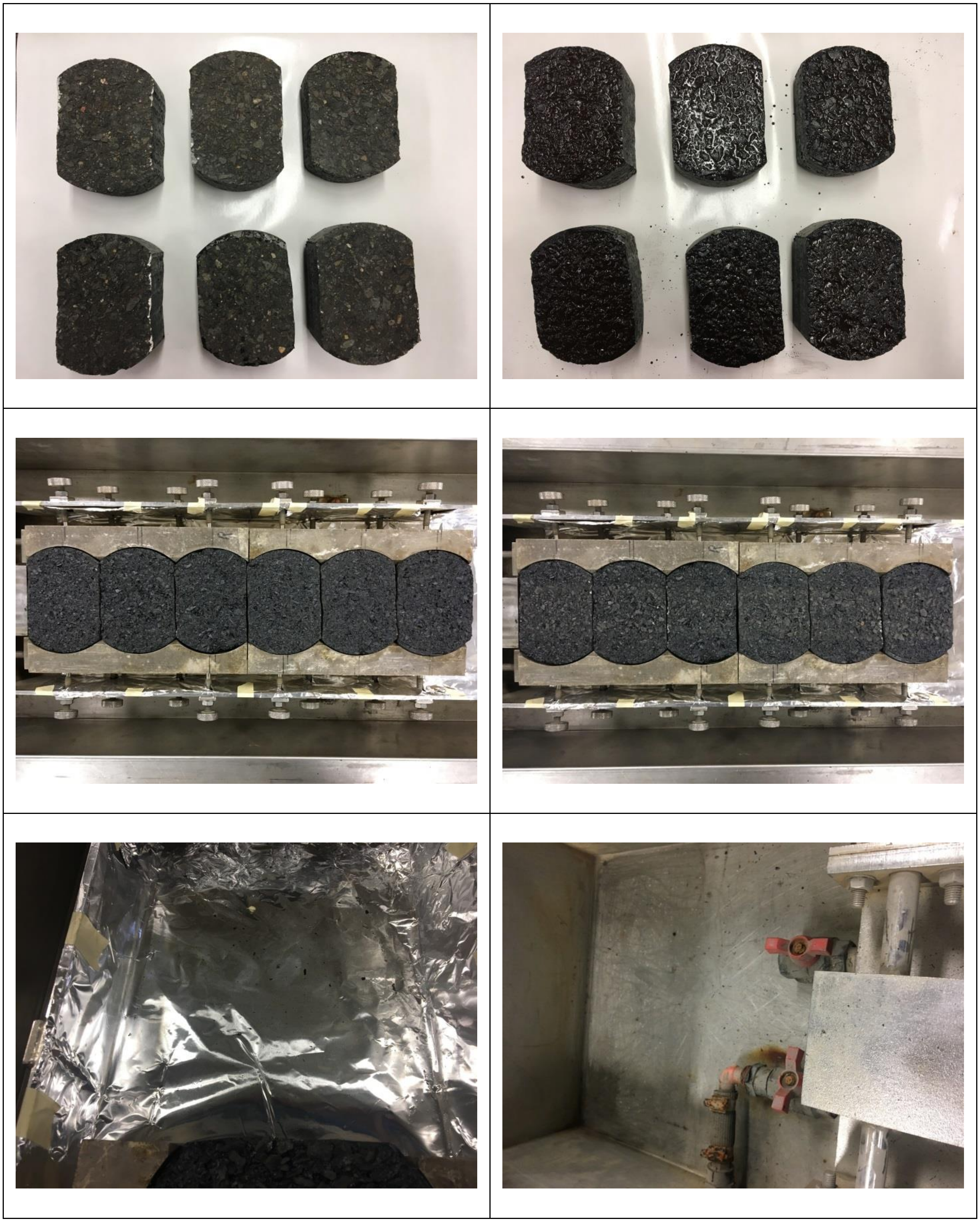

Figure C-17: Asphalt-Based, 48 Hour Cure Time, Test #2

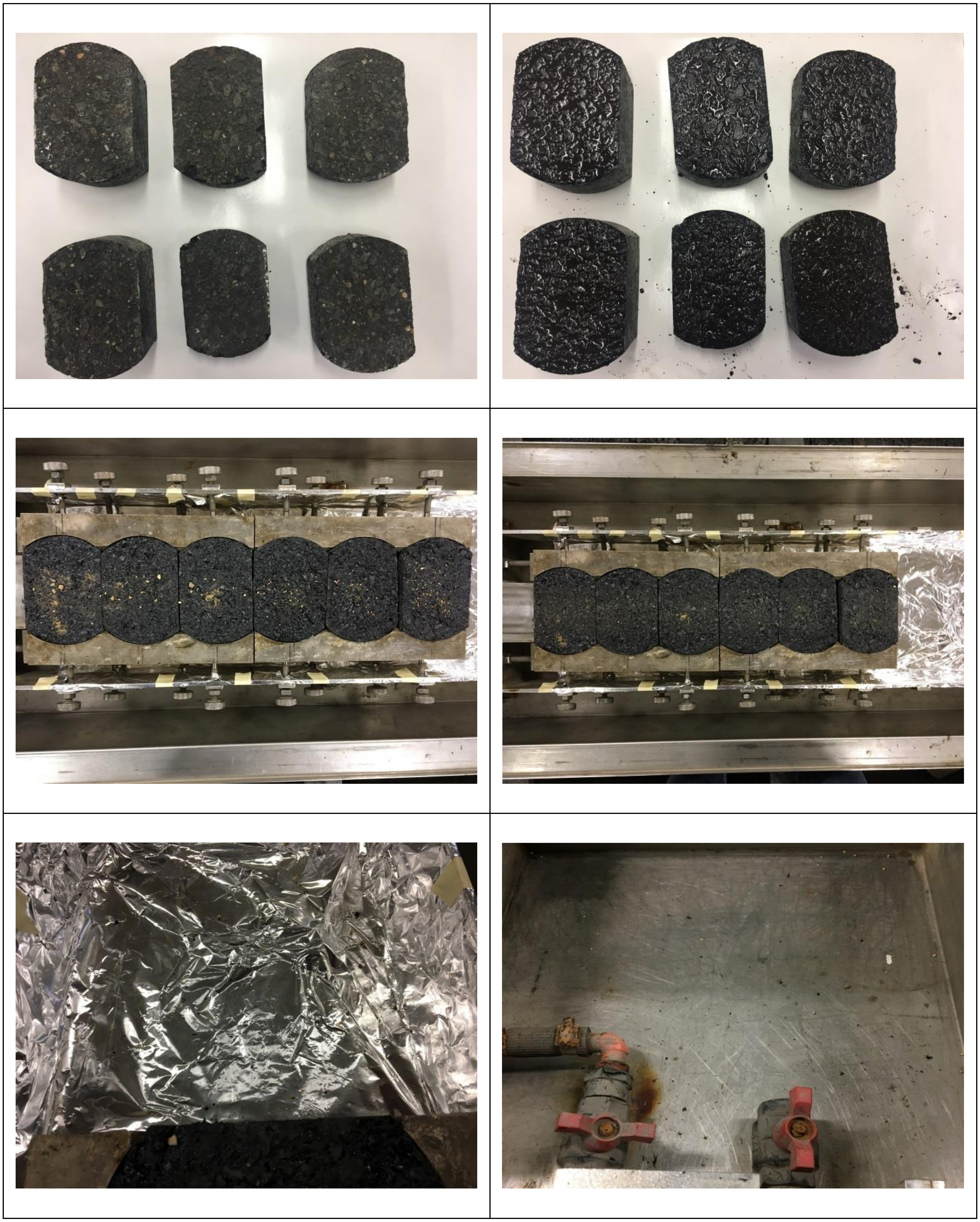

Figure C-18: Asphalt-Based, 48 Hour Cure Time, Sand Application, Test #1

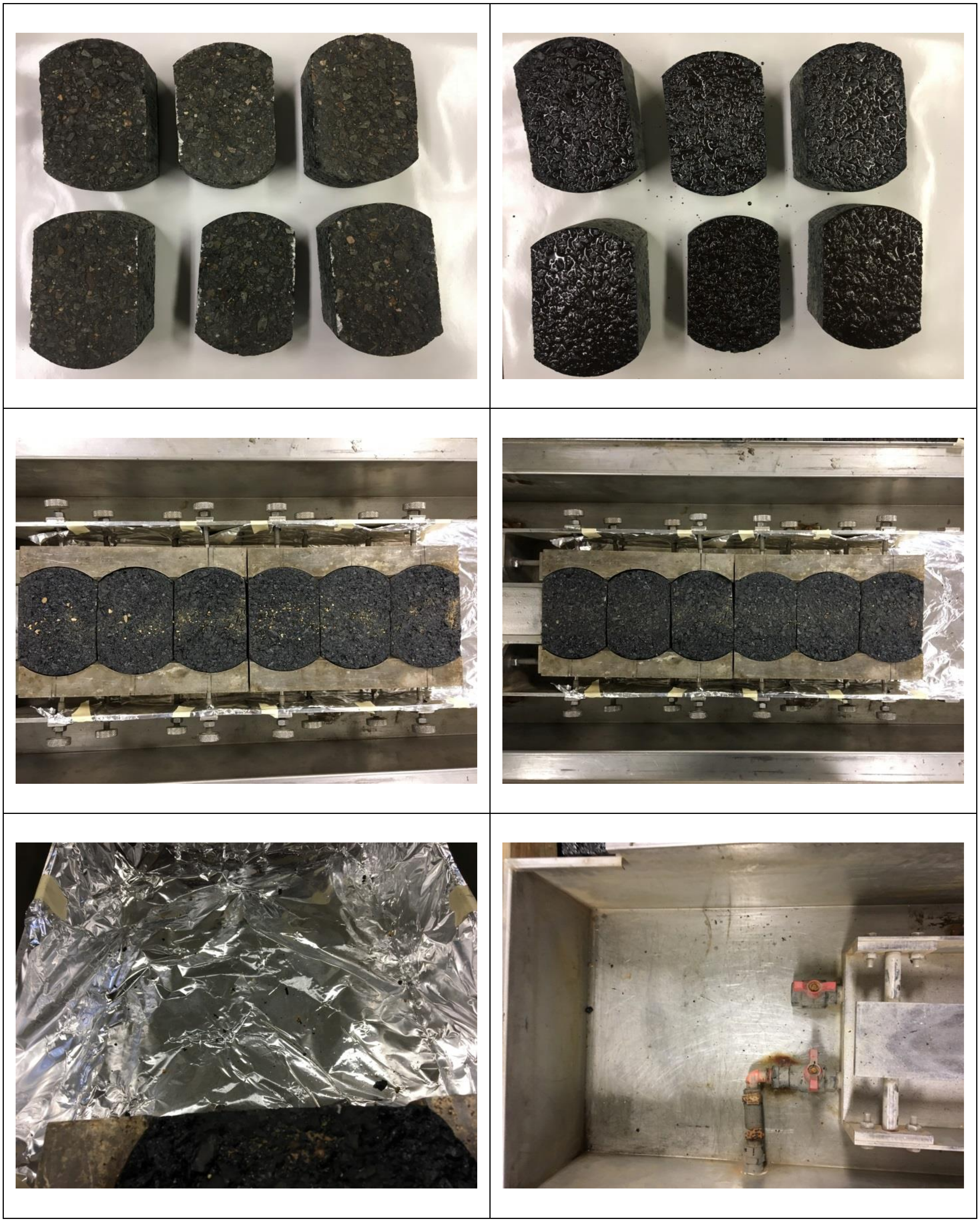

Figure C-19: Asphalt-Based, 48 Hour Cure Time, Sand Application, Test #2

Appendix D Chromatographs

The following appendix contains chromatograms for each external standard used and from each test completed.

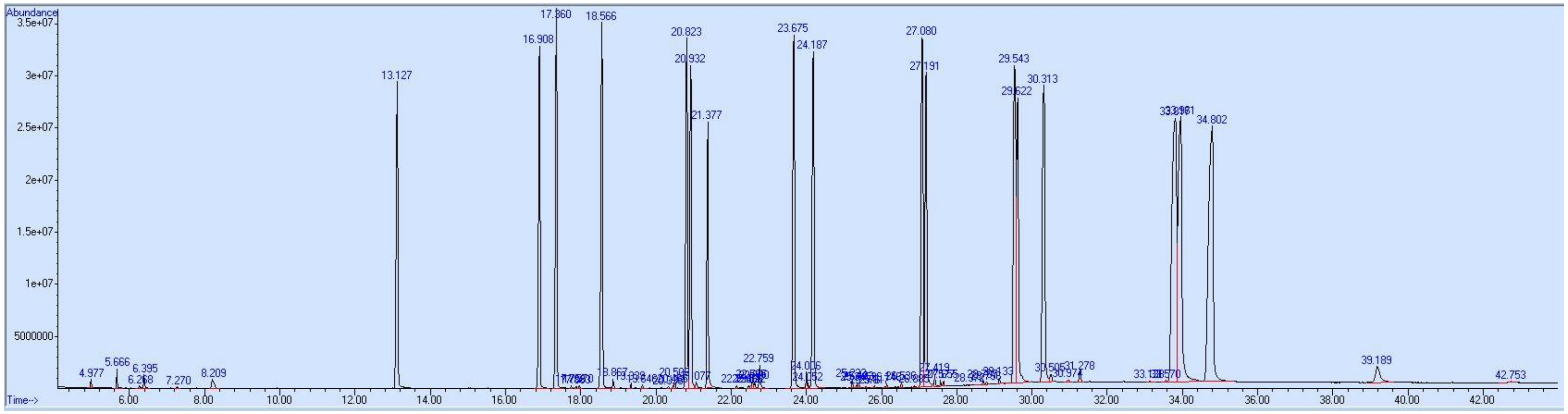

Figure D-1: Calibration Curve, 16 PAHs at 20 ppm & Carbazole at 10 ppm

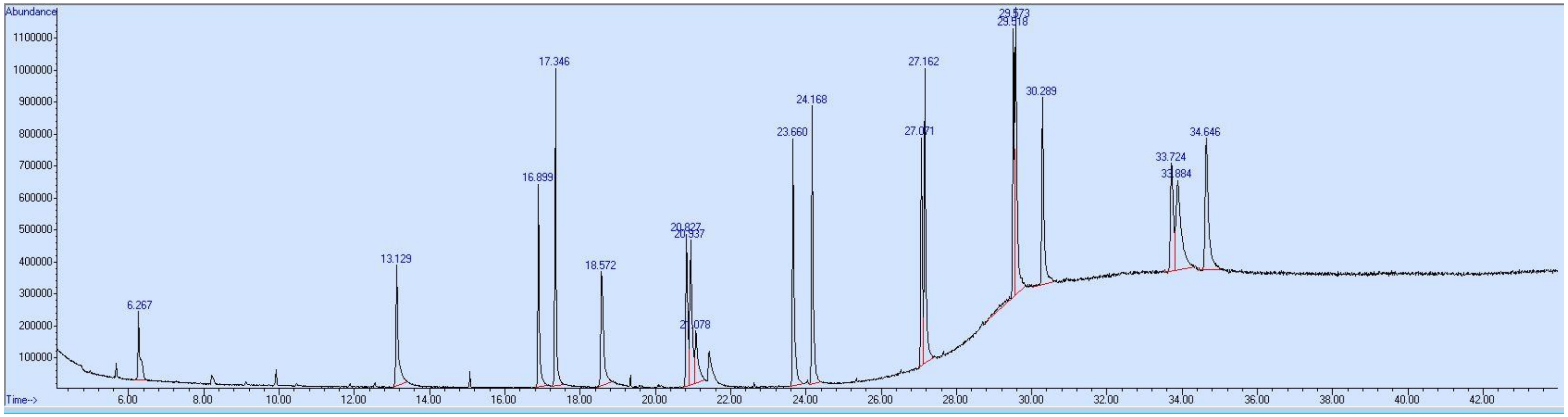

Figure D-2: Calibration Curve, 16 PAHs at 2 ppm & Carbazole at 1 ppm

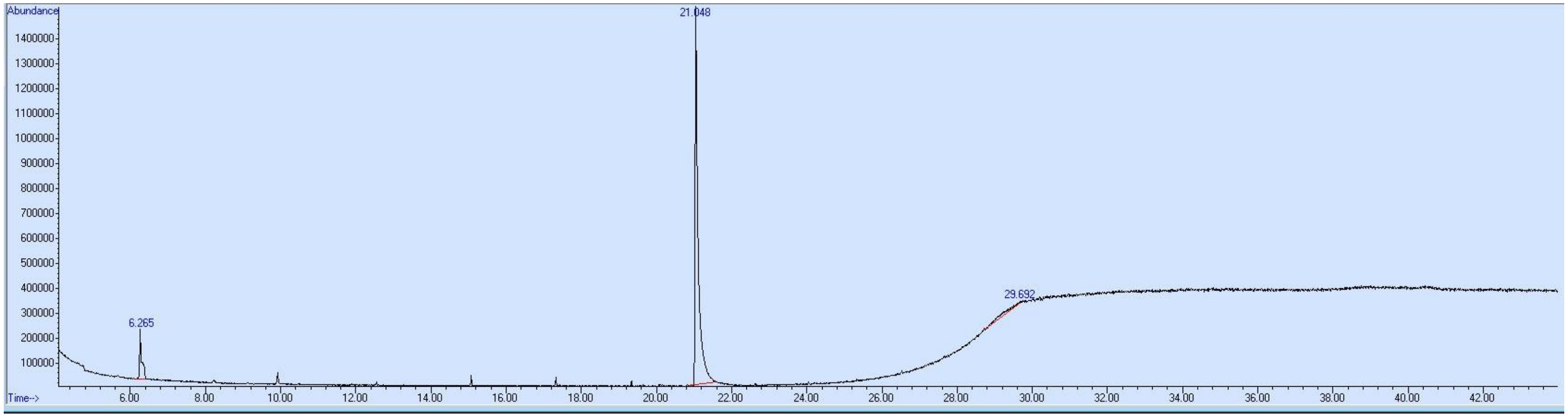

Figure D-3: Calibration Curve, Acridine at 1 ppm

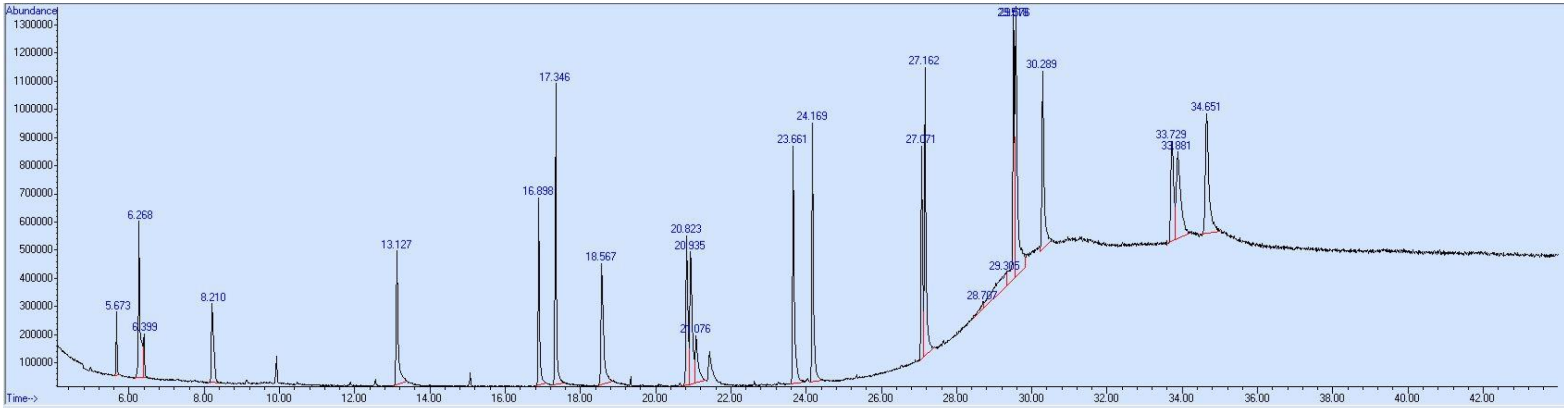

Figure D-4: External Calibration Curve, 16 PAHs at 0.2 ppm, Acridine and Carbazole at 0.1 ppm

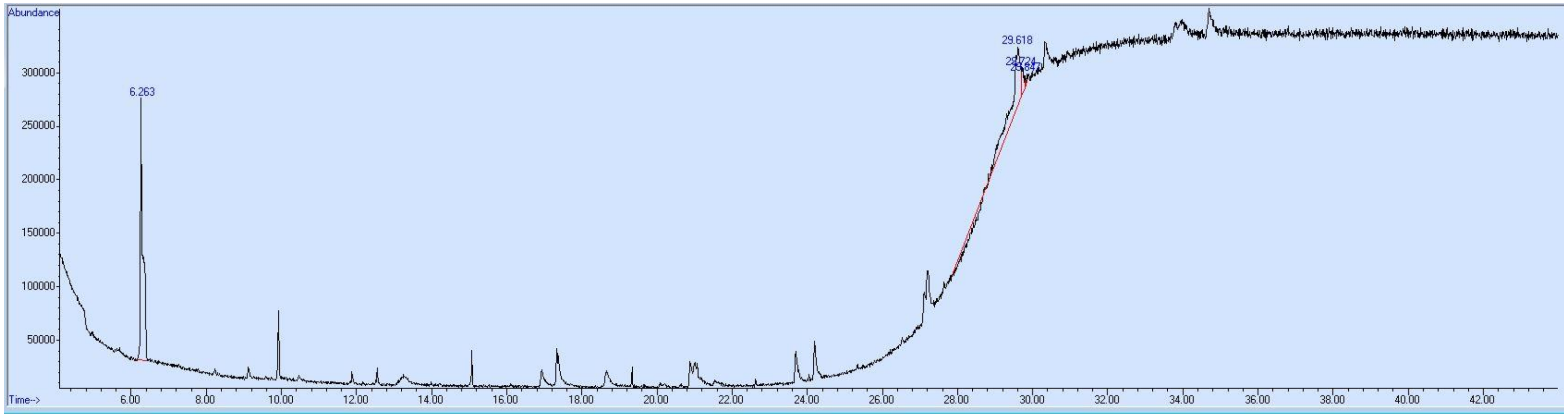

Figure D-5: External Calibration Curve, 16 PAHs at 0.02 ppm, Acridine and Carbazole at 0.01 ppm

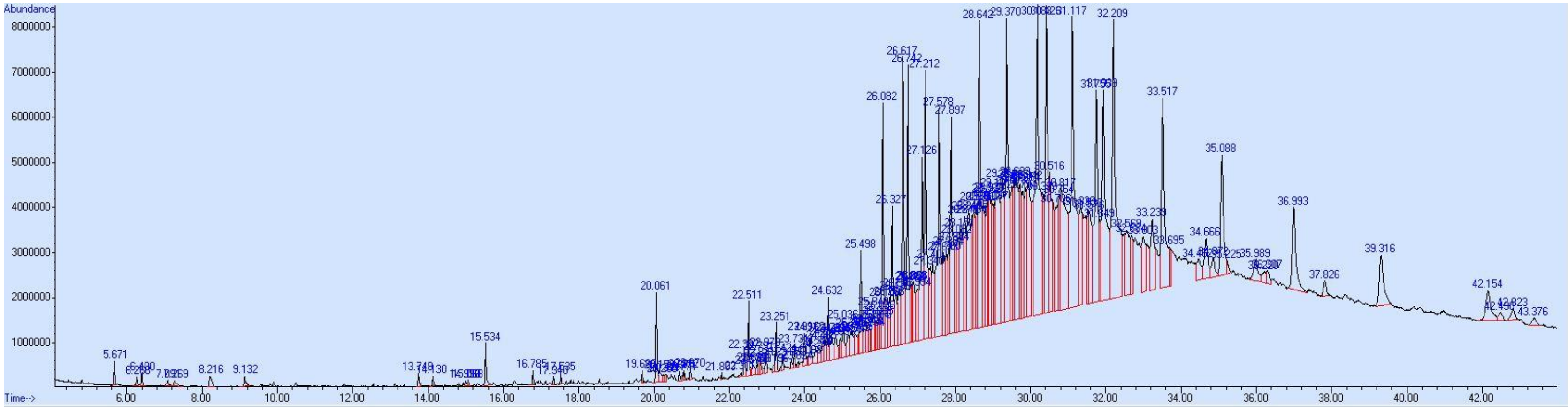

Figure D-6: Control Test #1 Chromatograph

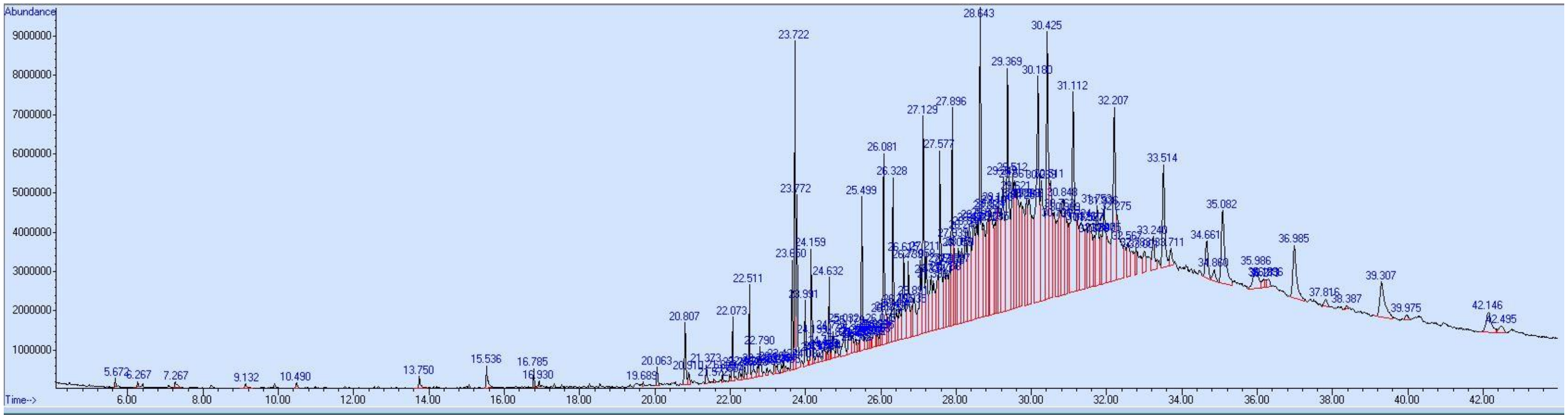

Figure D-7: Control Test #2 Chromatograph

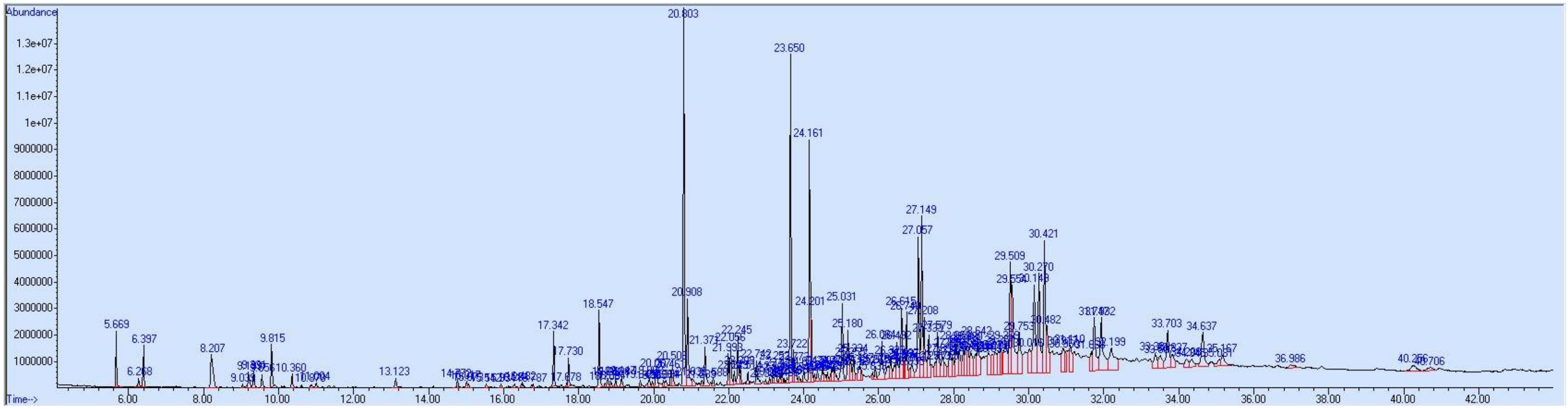

Figure D-8: Coal-Tar-Based, 48 Hour Cure Time, Test #1 Chromatograph

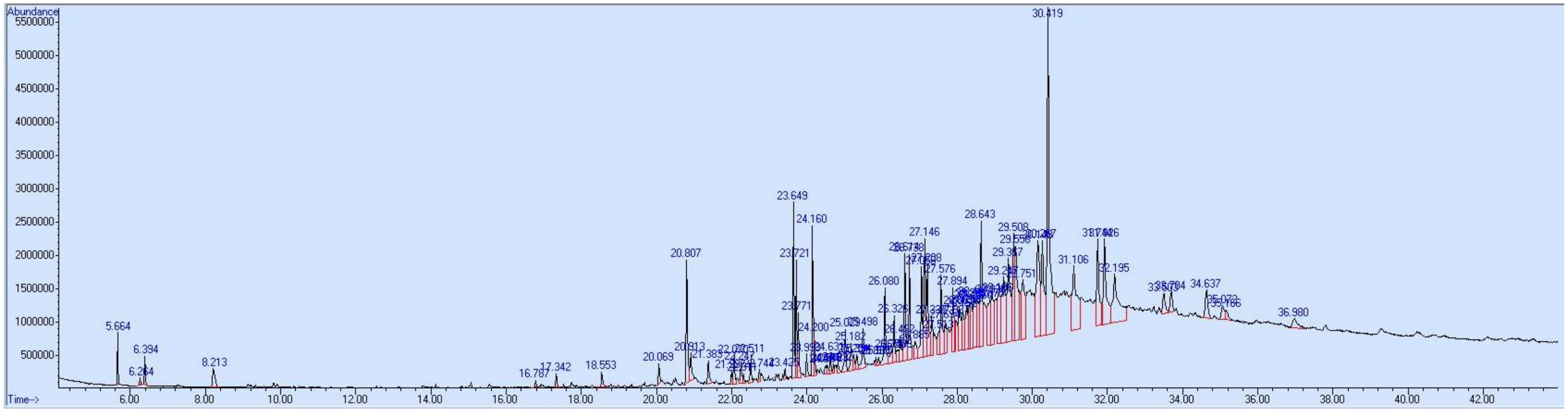

Figure D-9: Coal-Tar-Based, 48 Hour Cure Time, Test #2 Chromatograph

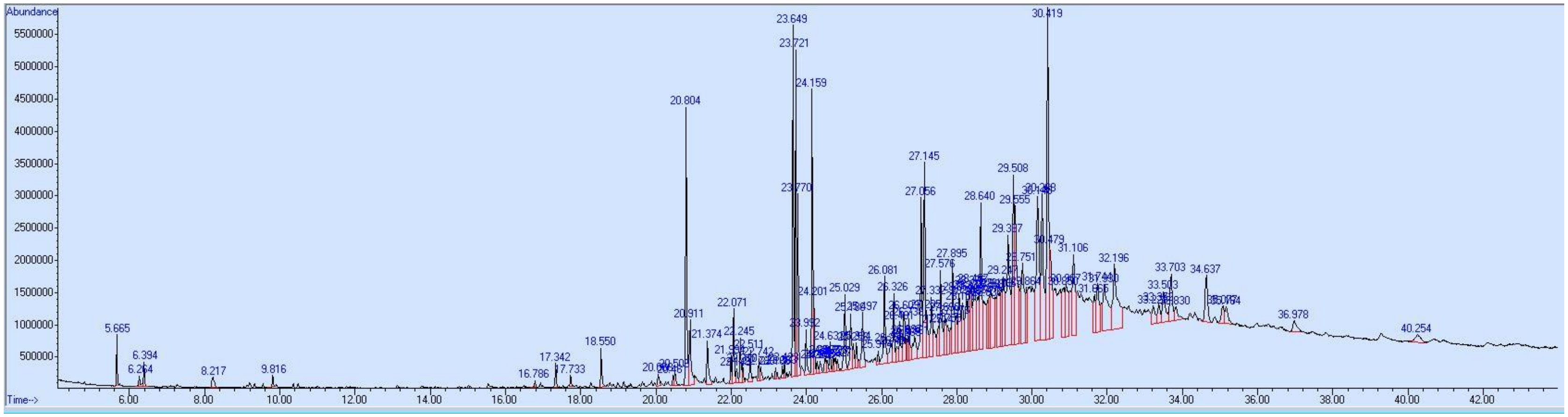

Figure D-10: Coal-Tar-Based, 48 Hour Cure Time, Test #3 Chromatograph

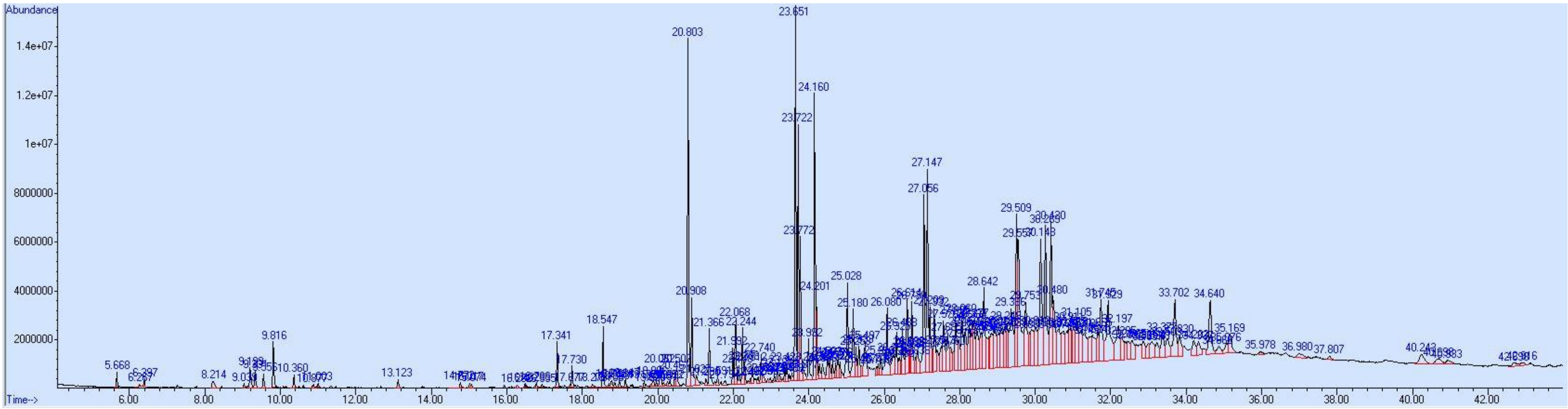

Figure D-11: Coal-Tar-Based, 3 Week Cure Time, Test #1 Chromatograph

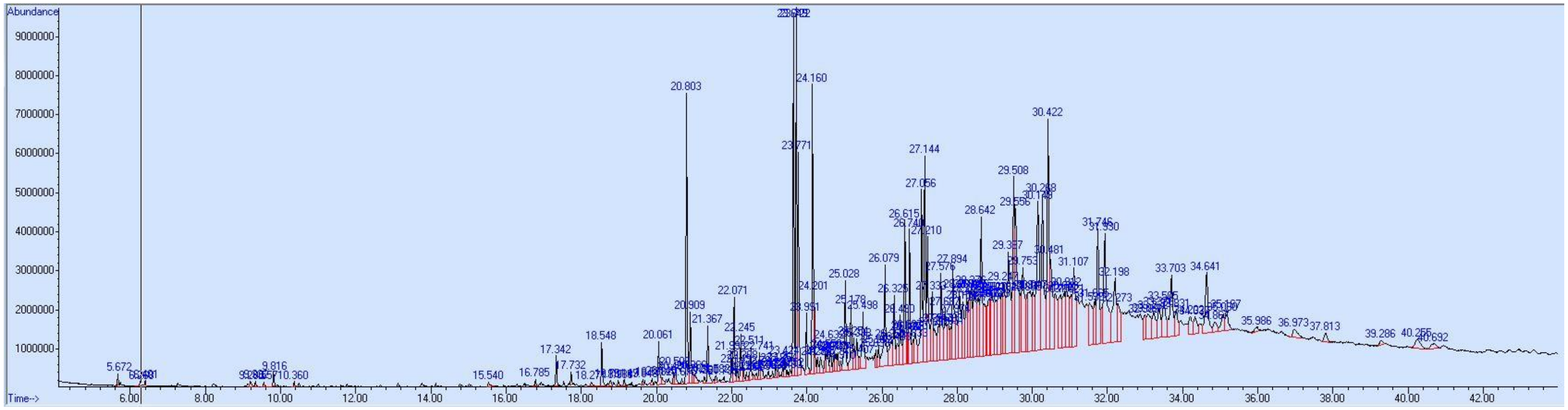

Figure D-12: Coal-Tar-Based, 3 Week Cure Time, Test #2 Chromatograph

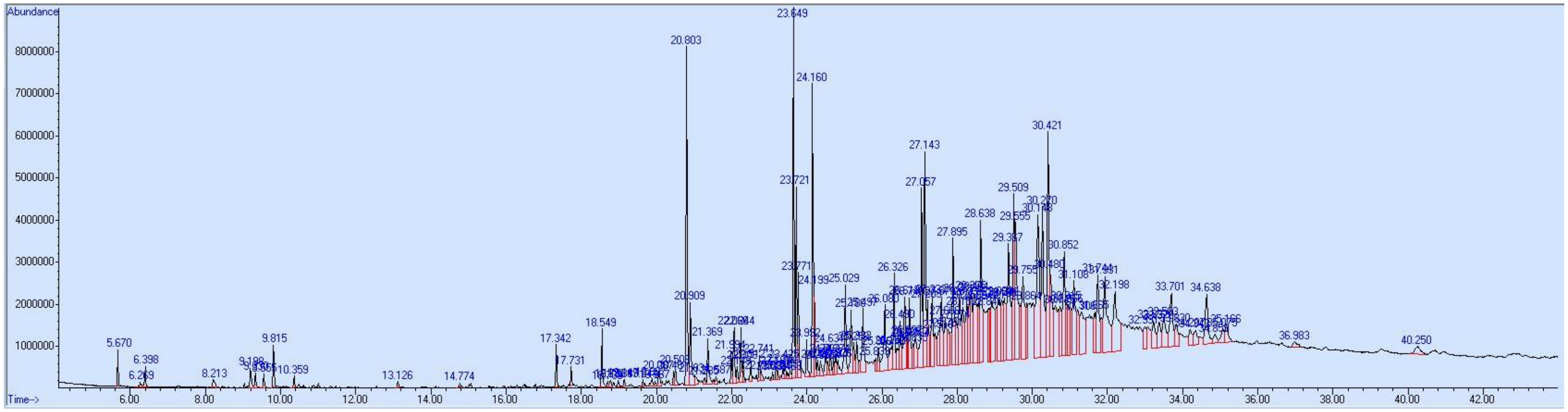

Figure D-13: Coal-Tar-Based, 48 Hour Cure Time, Sand Application Test #1 Chromatograph

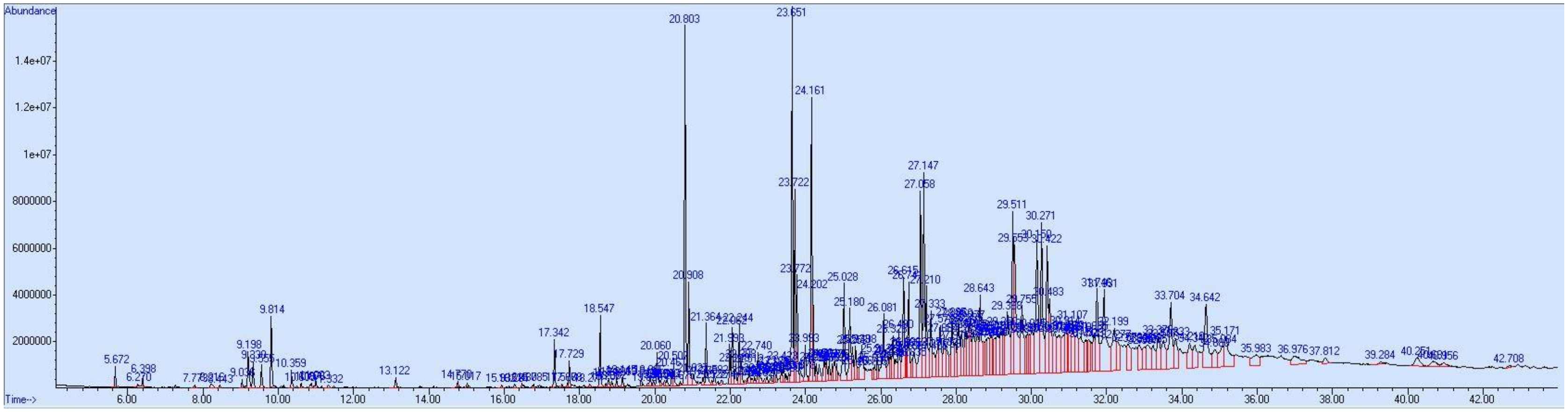

Figure D-14: Coal-Tar-Based, 48 Hour Cure Time, Sand Application Test #2 Chromatograph

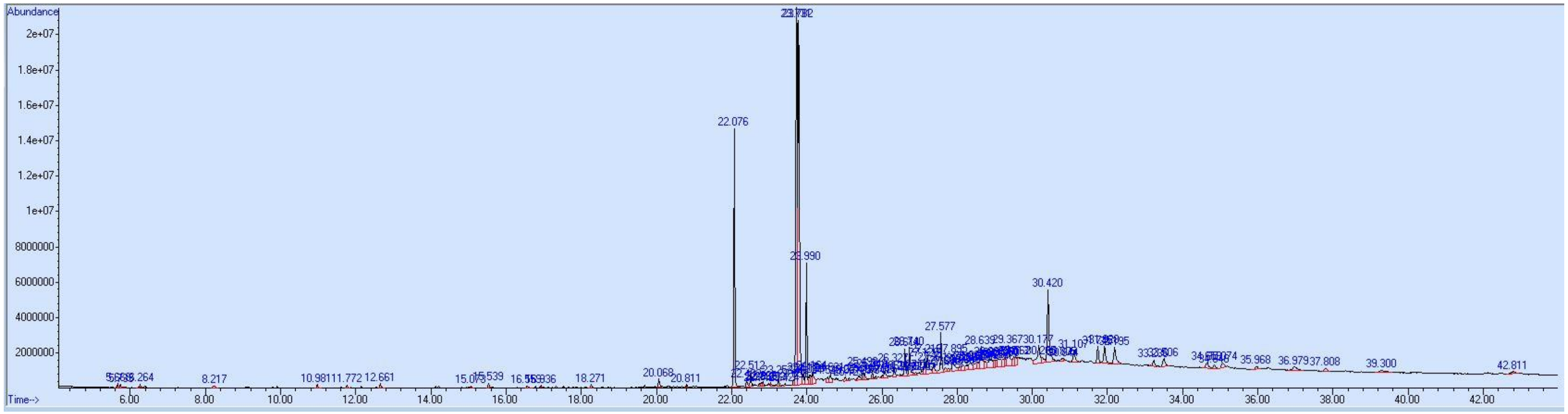

Figure D-15: Bio-Based, 48 Hour Cure Time, Test #1 Chromatograph

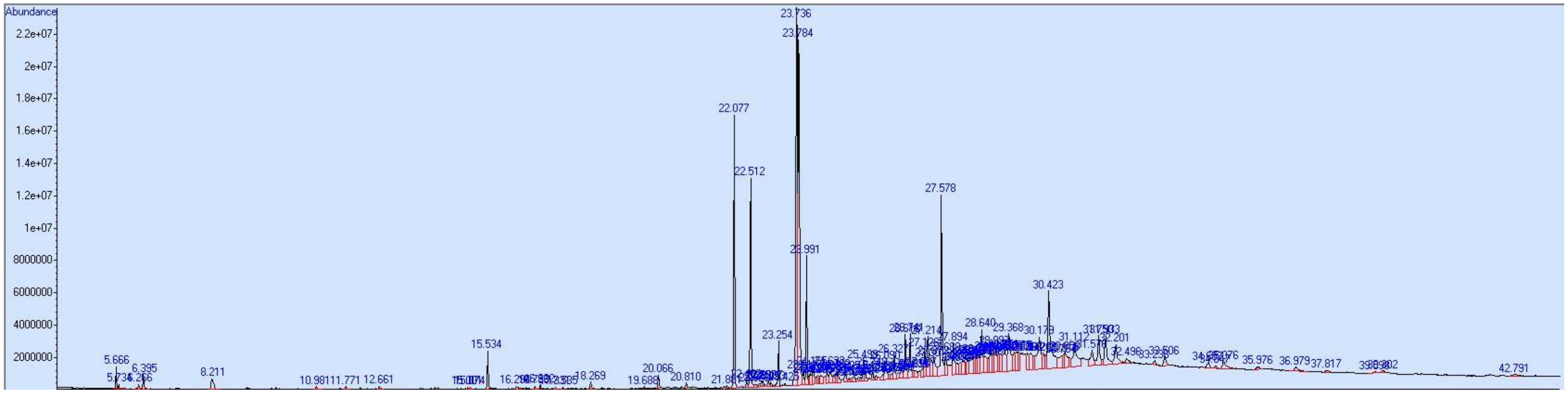

Figure D-16: Bio-Based, 48 Hour Cure Time, Test #2 Chromatograph

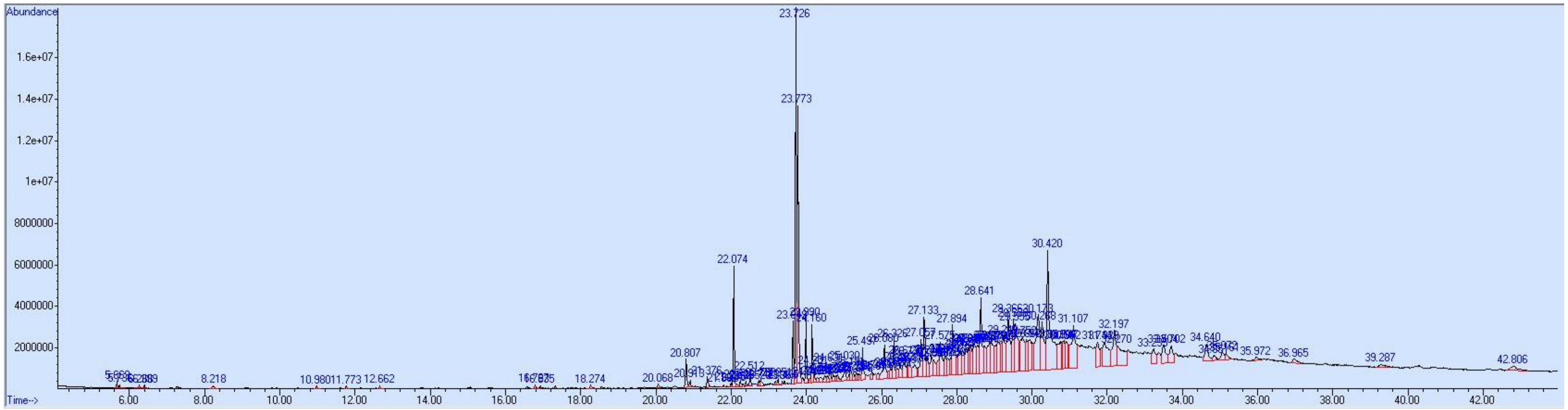

Figure D-17: Bio-Based, 3 Week Cure Time, Test #1 Chromatograph

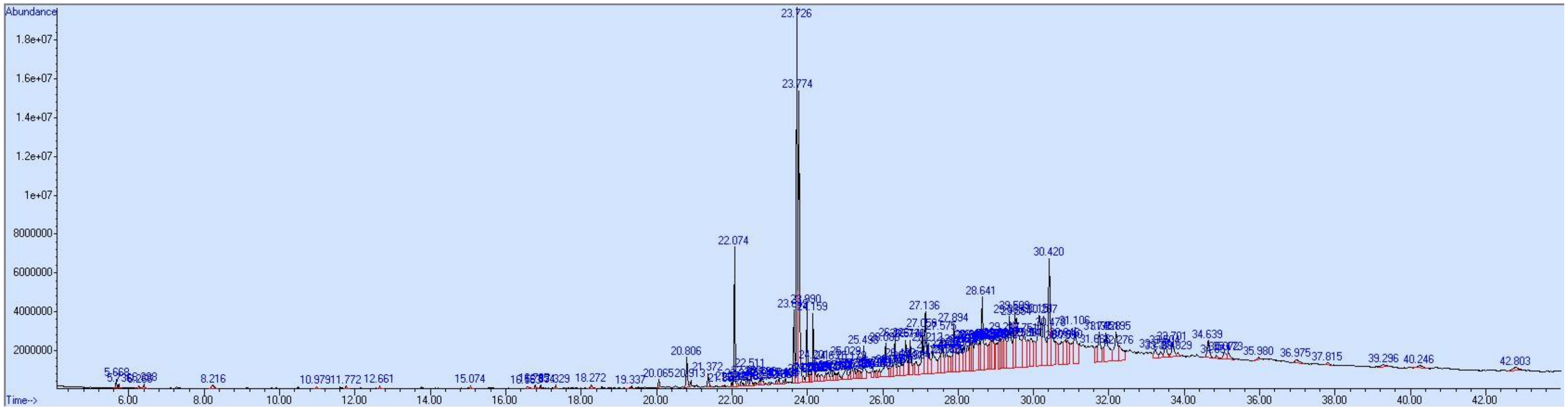

Figure D-18: Bio-Based, 3 Week Cure Time, Test #2 Chromatograph

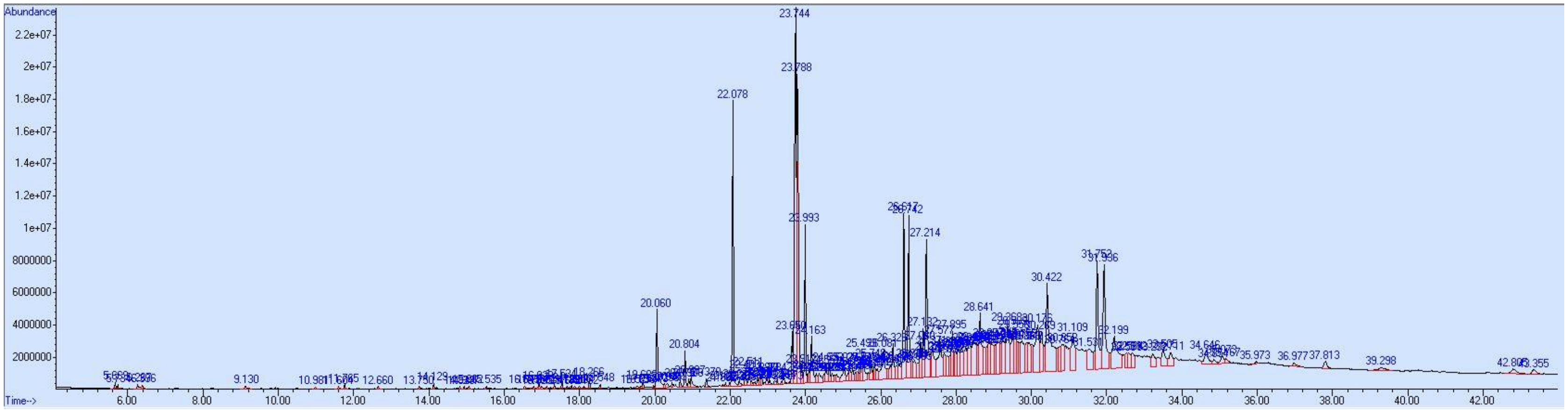

Figure D-19: Bio-Based, 48 Hour Cure Time, Sand Application Test #1 Chromatograph

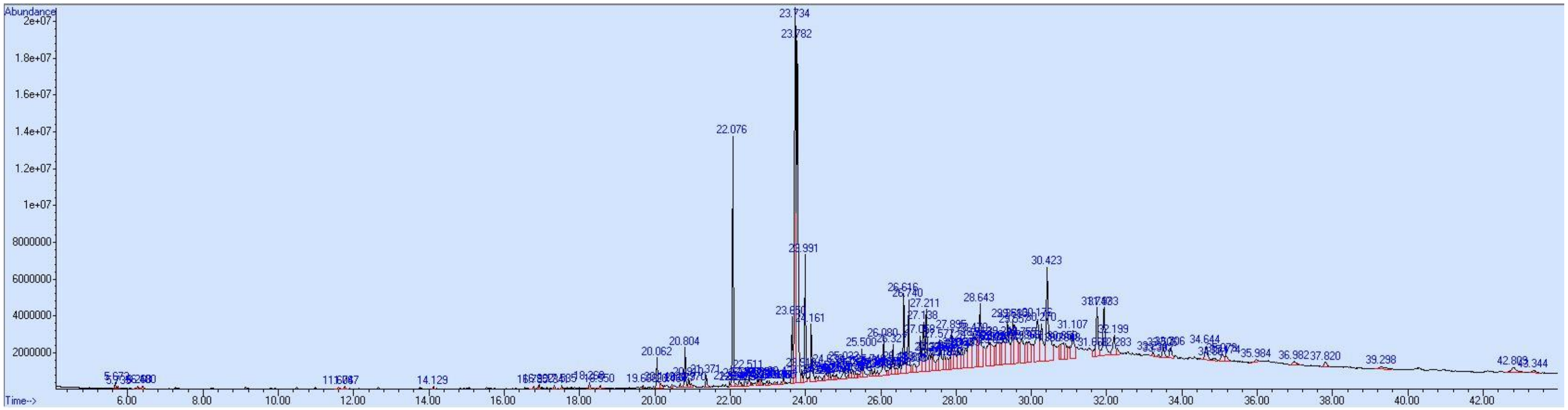

Figure D-20: Bio-Based, 48 Hour Cure Time, Sand Application Test #2 Chromatograph

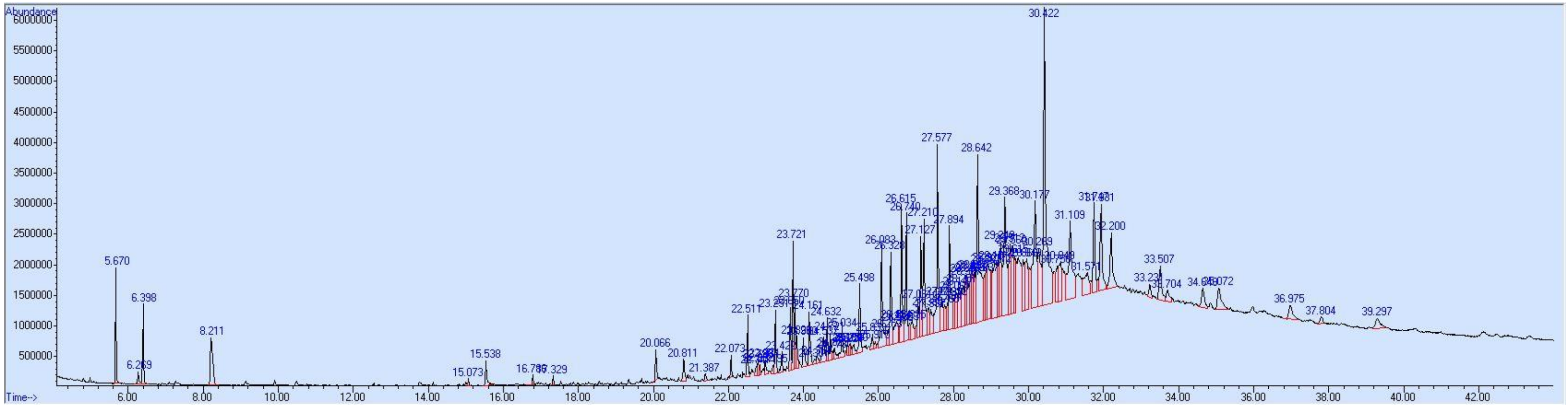

Figure D-21: Asphalt-Based, 48 Hour Cure Time, Test #1 Chromatograph

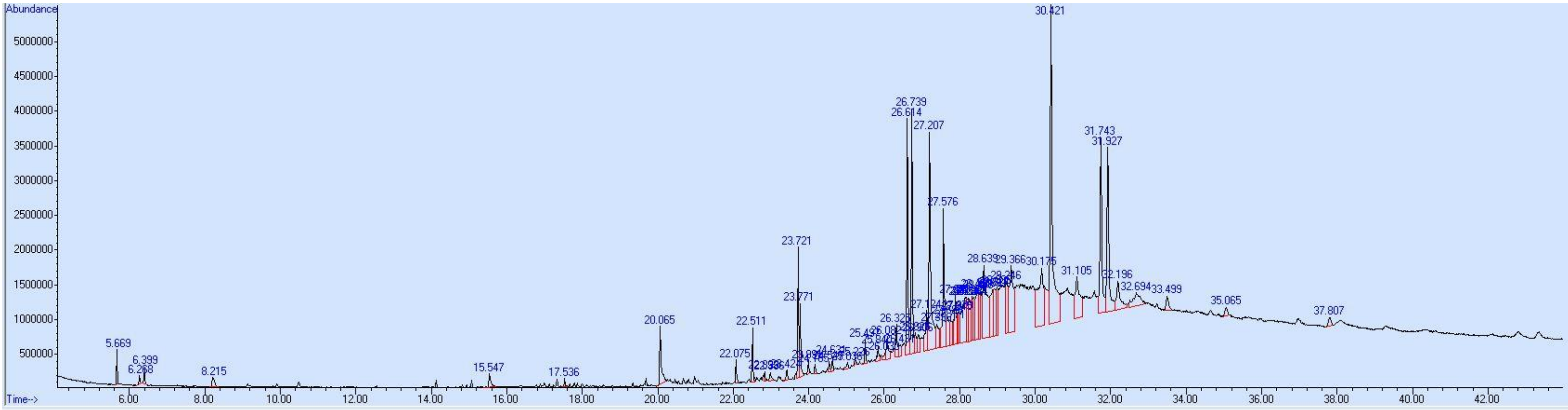

Figure D-22: Asphalt-Based, 48 Hour Cure Time, Test #2 Chromatograph

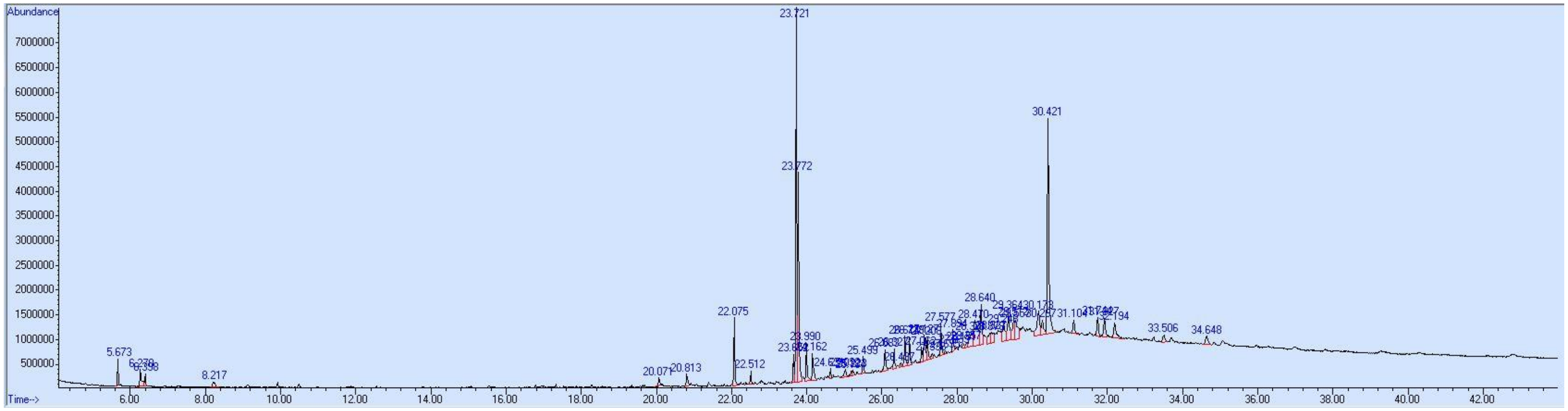

Figure D-23: Asphalt-Based, 48 Hour Cure Time, Sand Application Test #1 Chromatograph

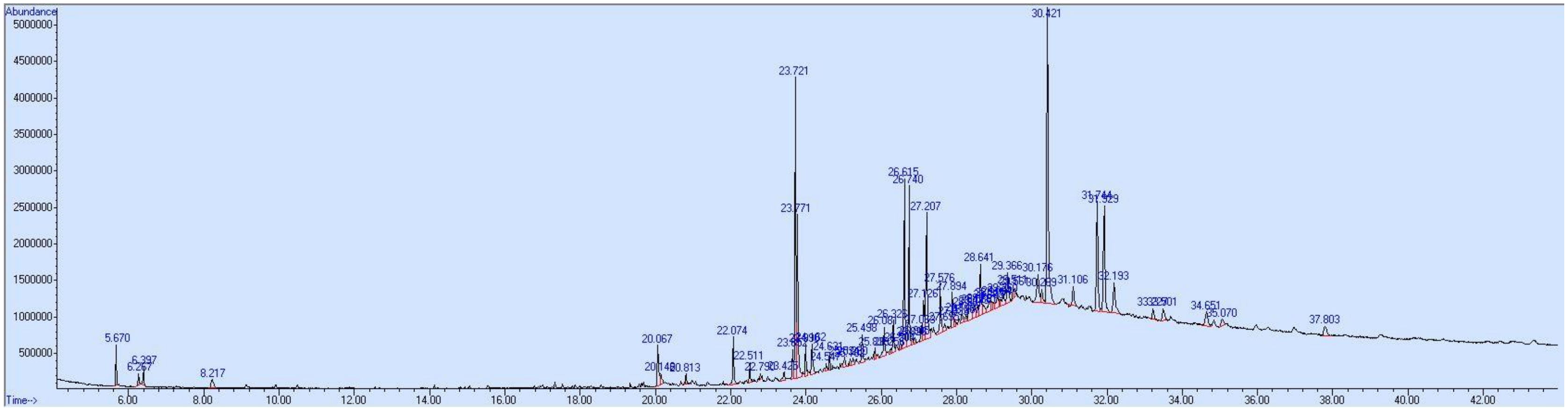

Figure D-24: Asphalt-Based, 48 Hour Cure Time, Sand Application Test #2 Chromatograph