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TECHNICAL NOTE

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How Long After Waterproofing a Deck Can You Still Isolate an Ignitable Liquid?

ABSTRACT: Dried, treated wood was sealed with Thompson's WaterSeal® "Clear Multi-Surface Waterproofer" and exposed to outdoor, summer conditions. Sections of the sealed wood were then periodically tested and analyzed in accordance with ASTM methods. The WaterSeal® contained a medium petroleum distillate (MPD) as a solvent for a wax. The treated lumber contained a background of aldehydes that could mimic a dearomatized MPD if not carefully investigated by the analyst. The MPD of the WaterSeal® was detectable 14 days, but not 27 days after application with exposure to relatively hot, dry and sunny weather conditions. The test was repeated with the MPD detectable 16 days, but not 20 days after application with exposure to cooler and wetter weather conditions. The testing demonstrates the need for a thorough and complete investigation by the fire investigator and the submission of comparison samples to the laboratory.

KEYWORDS: forensic science, criminalistics, fire debris, gas chromatography, mass spectrometry, GC-MS, waterproof, wood decking, petroleum distillate, comparison samples

Many waterproofing products for wood, brick and concrete, commonly called "sealers," consist of a wax dissolved in a medium petroleum distillate (such as mineral spirits). The medium petroleum distillate (MPD) penetrates the wood, brick or concrete, carrying the wax within. Once the MPD dissipates, the wood, brick or concrete is left with a wax coating that slightly penetrates the surface and makes the surface "water proof." Over time, with exposure to wind, sun and precipitation, the wax coating is worn off and the surface requires re-sealing.

In fire investigation, MPD products are considered ignitable liquids that can be used to accelerate a fire. MPD products are present in a wide variety of consumer products (1,2). While there are many consumer products that contain MPD products, a common source the fire investigator encounters stored in or around residential decks are charcoal lighter fluids. With residential decks being sealed with waterproofing products, many of which use MPD products in their formulation, and decks having charcoal lighter fluids commonly stored in the area, the fire investigator must be knowledgeable about other sources of MPD products associated with decks.

While the persistence of floor coating solvents has been investigated in an indoor setting (3), this investigation was performed in order to determine how long the ignitable liquid component of a sealer could still be detected after it had been applied to treated lumber and exposed to outdoor weather conditions. Treated lumber was chosen as the test matrix since it is widely used in residential decks, and would probably be the most commonly sealed product that could become the focus of a fire investigation.

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Method

The test specimen was a 5 cm × 15 cm × 244 cm (2″ × 6″ × 8′) piece of Wolmanized® treated pine lumber that had been stored in a dry area out of direct sunlight for at least two years. The piece of wood was ripped in half lengthwise and a 18 cm (7 in.) length was removed from the end of both boards for background testing. The two long pieces of wood were placed parallel to one another approximately 2 cm (¾ in.) apart with the finished edges facing one another in order to reproduce the spacing found on decks. The parallel lengths of treated lumber were supported approximately 9 cm (3.5 in.) over a concrete sidewalk. One coat of Thompson's WaterSeal® "Clear Multi-Surface Waterproofer" was applied to the two long planks according to product specifications. The sealed wood planks were placed where they were continually exposed to the weather and would be in direct sunlight for most of the daylight hours.

Periodically, 18 cm (7 in.) lengths from the ends of both of the sealed wood planks were removed and prepared for analysis in accordance with ASTM E 1412 (4), and then analyzed in accordance with ASTM E 1618 (5). Specifically, the two lengths of sealed wood were both placed in a new unlined gallon paint can along with a DFLEX device (Albrayco Laboratories, Inc., 38 River Road, Cromwell, CT). Each can was then placed in an 80°C (176°F) oven for approximately 5 h. The activated charcoal strip was removed from the DFLEX device, placed into a GC vial, desorbed with 0.5 mL of carbon disulfide and analyzed using gas chromatography-mass spectrometry (GC-MS). Test samples of sealed wood were removed and tested 1, 5, 14, and 27 days after application of the sealer.

The 18 cm lengths of wood planks collected prior to sealer application were similarly prepared and analyzed for background testing. Also for background testing, a new paint can containing only 10 μL of the Thompson's WaterSeal® "Clear Multi-Surface

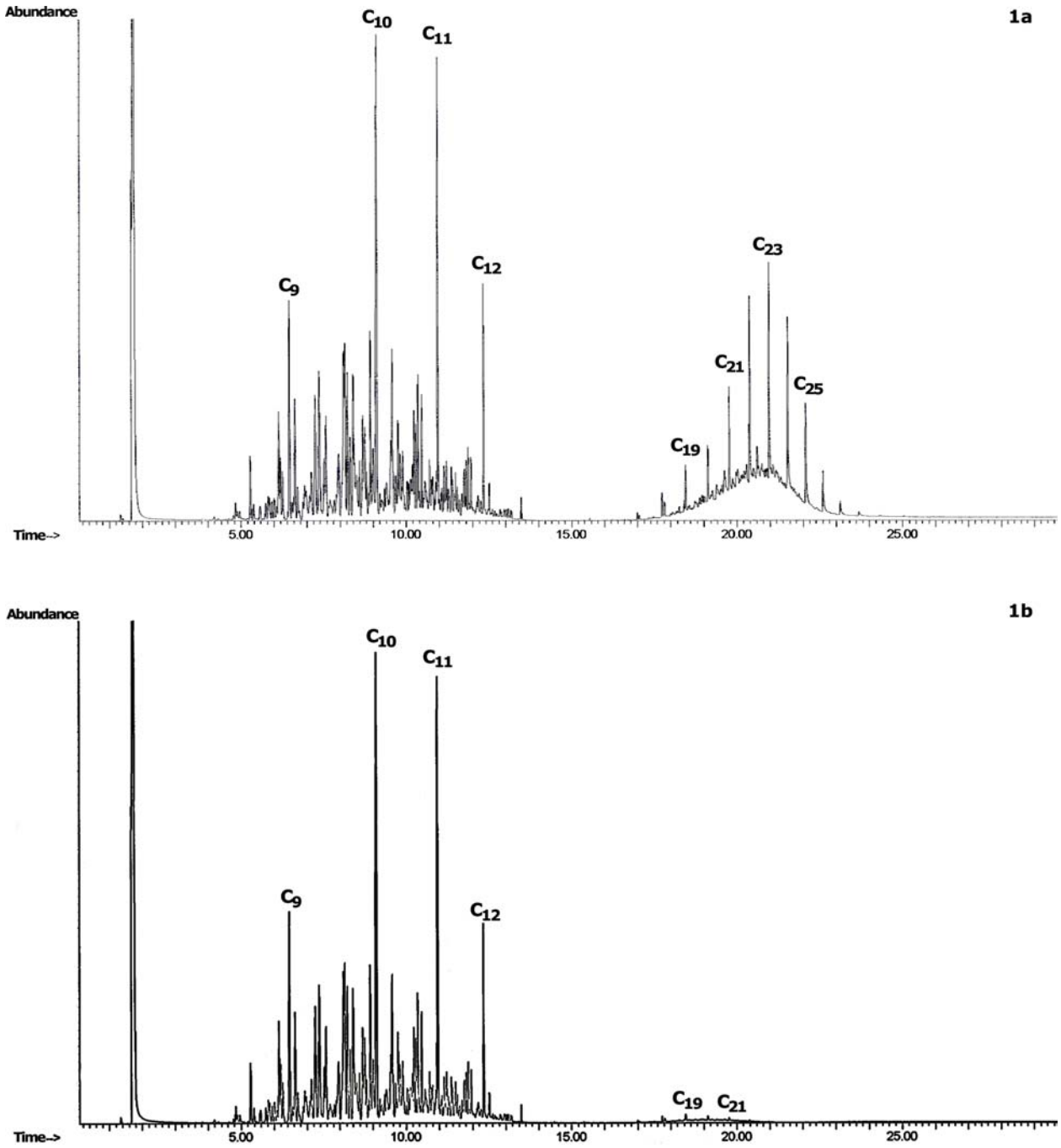

FIG. 1—*The total ion chromatogram of Thompson's WaterSeal® "Clear Multi-Surface Waterproofer" when directly diluted and analyzed (1a) and when analyzed by passive headspace concentration (1b). The straight chain hydrocarbons are noted by the letter "C" and the number of carbons in the chain (e.g., decane is represented by "C_{10}").*

Waterproofer" was similarly prepared and analyzed. For comparison, 10 uL of the WaterSeal® was directly diluted into 0.5 mL of carbon disulfide and analyzed by GC-MS.

Forty days after the initial coat of sealer was applied to the wood, another coat of Thompson's WaterSeal® "Clear Multi-Surface Waterproofer" was added to what remained of the planks and the sampling and analysis procedure was repeated as described above. Sample lengths of wood were removed and tested as described above at intervals of 5, 9, 12, 16 and 20 days after application of the second coat of WaterSeal®.

GC-MS Operating Parameters

All samples were analyzed using a Hewlett-Packard 6890 gas chromatograph with a Hewlett-Packard Model 5973 mass selective detector (Hewlett-Packard/Agilent, Wilmington, Delaware). The column was a 0.25 μm film SPB-5 column, 30 m × 0.25 m (Supelco, Bellefonte, PA). The carrier gas was helium at a constant flow of 1.0 mL/min. All samples were tested by injecting a 2 μL sample, split 20:1, at 250°C. The oven temperature program was held at the initial temperature of 45°C for 1 min, ramped to 80°C at 5°C per minute and then immediately ramped to 300°C at 15°C per minute

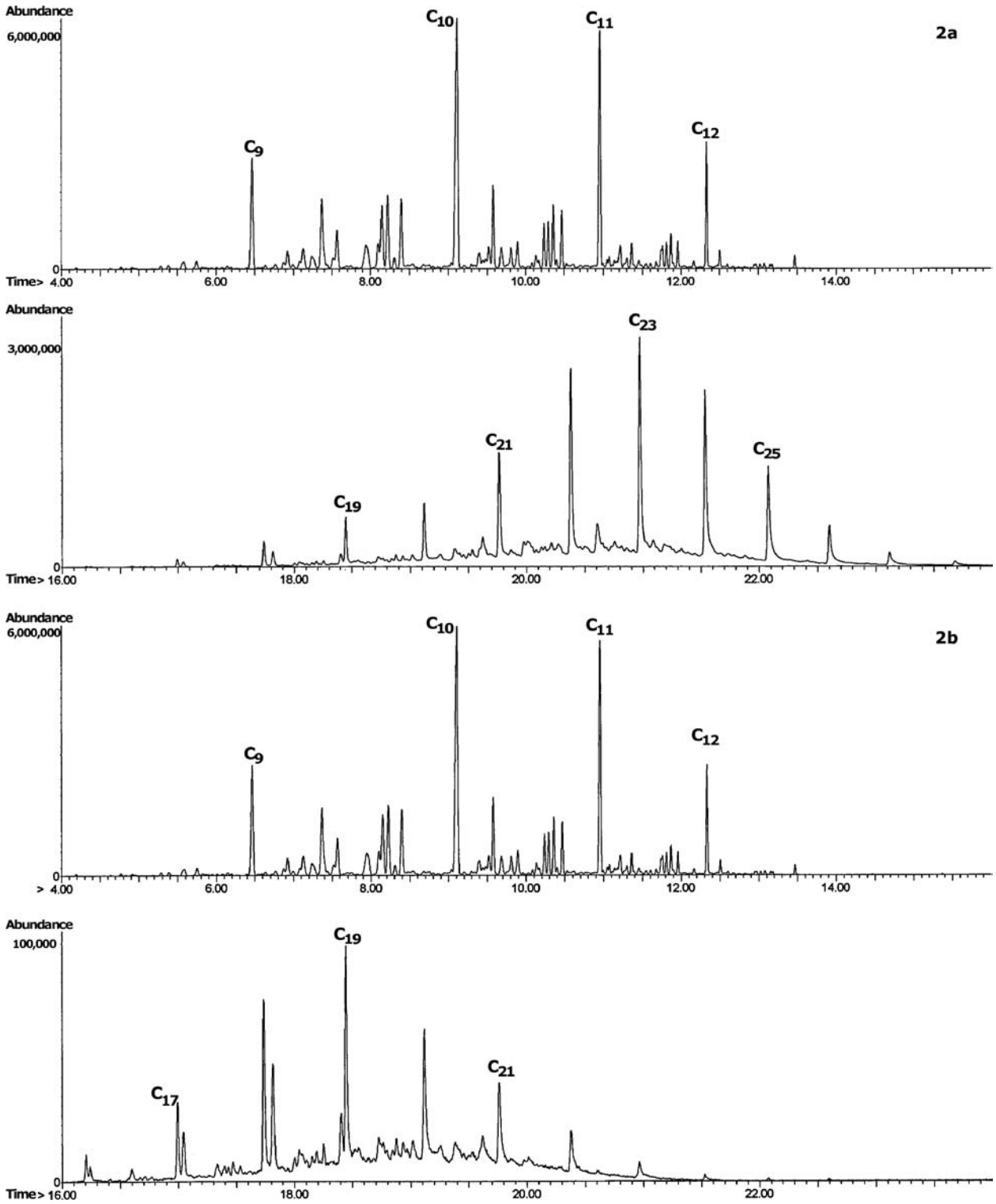

FIG. 2—*The alkane mass chromatogram (sum of ions 43, 57, 71, and 85) of Thompson's WaterSeal® "Clear Multi-Surface Waterproofer" when directly diluted and analyzed (2a) and when analyzed by passive headspace concentration (2b). The straight chain hydrocarbons are noted by the letter "C" and the number of carbons in the chain (e.g., decane is represented by "C_{10}").*

and held at 300°C for 7 min. Ions were scanned from 20 to 400 AMU.

Results

Analysis of the direct dilution and analysis of the Thompson's WaterSeal® product used showed the product contained a medium petroleum distillate (MPD) ignitable liquid with the maximum response in the normal alkane range of C10 and C11, and a wax in the normal alkane range of C18 to C27 (see Fig. 1*a*). When passive headspace analysis of the product was performed, the medium petroleum distillate component of the WaterSeal® was the majority of that isolated (see Fig. 1*b*) due to the known fractionation of the passive headspace method (6–8). However, a minor response was

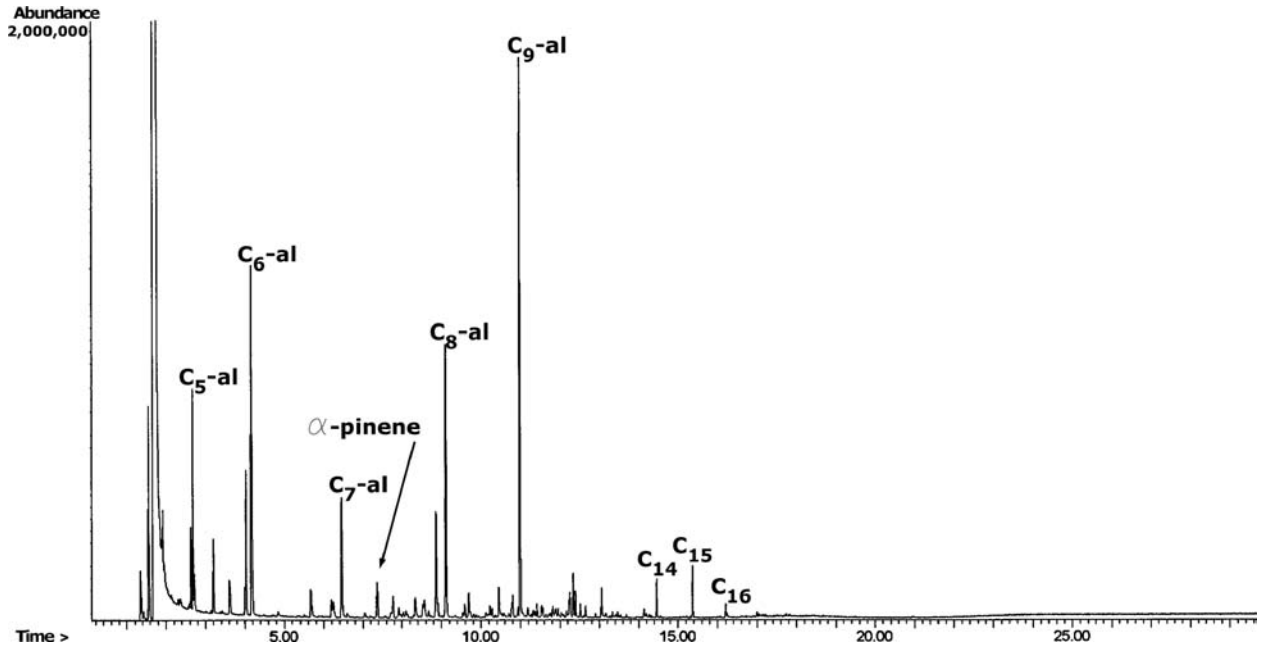

FIG. 3—*The total ion chromatogram obtained from the passive headspace analysis of the treated wood boards prior to any application of sealer. The straight chain aldehydes are indicated by the number of carbons in the chain followed by "-al" (e.g., hexanal is represented by "C_6-al").*

generated by the wax component and observed in the normal alkane range of C17 to C22. Figure 2 highlights the fractionation of the WaterSeal® product when the passive headspace method is used. Review of the combined alkane mass chromatograms of the passive headspace analysis (Fig. 2*b*) in the wax area showed a significantly lower response than the direct dilution analysis. Also, note the change in the alkane pattern distribution above C16 as compared to the direct dilution and analysis (Fig. 2*a*). The alkane profile in the passive headspace analysis of the wax portion (above C16) of the WaterSeal® (Fig. 2*b*) is approaching the profile obtained from some heavy petroleum distillates (e.g., diesel fuel).

The background analysis testing of the unsealed wood planks showed a major component pattern of straight chain aldehydes (pentanal, hexanal, heptanal, octanal, and nonanal) and a minor pattern for the normal alkanes C14, C15, and C16 (see Fig. 3). It is supposed that the aldehydes are a result of the process used to treat the wood; either as additives or breakdown products produced in the Wolmanizing® process.

In order to replicate laboratory interpretation parameters while analyzing the data in this study, each GC-MS analysis result was interpreted as if the sample was an unknown submitted to the laboratory for ignitable liquid analysis. The fact that a sample was coated with sealer known to contain MPD was not used to influence the decision as to whether or not MPD was still present on the wood plank sections. In this way, a true time frame for MPD identification after application as it would apply in a real world sample was more accurately reproduced. Therefore, more data was reviewed than presented here when making the final determination as to whether or not the MPD was still present in the wood. Other factors investigated included response of the test samples as compared to a 0.05% sensitivity check standard of MPD (per ASTM E 1618), as well as individual peak mass spectral identifications.

In the first test, a MPD was isolated on the sealed wood samples 14 days after Waterseal® application but was not isolated on the wood 27 days after application. Figure 4 shows the total ion chromatogram of the test samples in the MPD range as the time from application of the WaterSeal® progressed. Note that the response from the MPD diminished over time and the aldehyde pattern from the wood background eventually overshadow the normal alkanes in the sample. Figures 5 and 6 show the alkane and the aromatic mass chromatographic patterns of the test samples as the time from application of the WaterSeal® progressed. Figure 5 illustrates how closely the retention times of the straight chain aldehydes in the treated lumber are to the retention times of the normal alkanes of the MPD under the conditions of analysis. This highlights the need for the analyst to thoroughly investigate each major peak in the combined mass chromatograms as the aldehydes and the straight chain alkanes of the MPD show a similar alkane mass chromatogram. While the aromatic pattern appears relatively intact after 27 days (Fig. 6), the alkane pattern (Fig. 5) of the MPD is becoming overrun by the aldehyde background and the overall response is low compared to 0.05% sensitivity check standards, thus resulting in a "negative" call.

Generally, the weather was hot and dry for the 27 day period of the first test. Based upon a summary of the NOAA National Climatic Data for the test period (9), the average high temperature was 30°C (86°F), the total amount of rainfall was less than 1.5 cm (0.6 in.) and there was 13 to 14 h of daylight each day. The sky had no cloud cover or was 25% covered with clouds or less approximately 36% of the daylight hours. The sky was completely cloud covered approximately 19% of the daylight hours. The overall average temperature over this 27 day period was 24°C (76°F) with a maximum of 34°C (94°F) and a minimum of 14°C (57°F) (9).

In the second test, chromatographic results were similar to the first test and showed that the medium petroleum distillate was isolated on the wood samples 16 days after application but was not isolated on the wood samples 20 days after application. Generally, the weather was cooler and wetter over the 20-day period of the second test. Based upon a summary of the NOAA, National Climatic Data for the test period (9), the average high temperature was 25°C (77°F), the total amount of rainfall was 9.4 cm (3.7 in.) and there was 11.3 to 12.3 h of daylight each day. The sky had no cloud cover or was 25% covered with clouds or less approximately 34% of the daylight hours. The sky was completely cloud

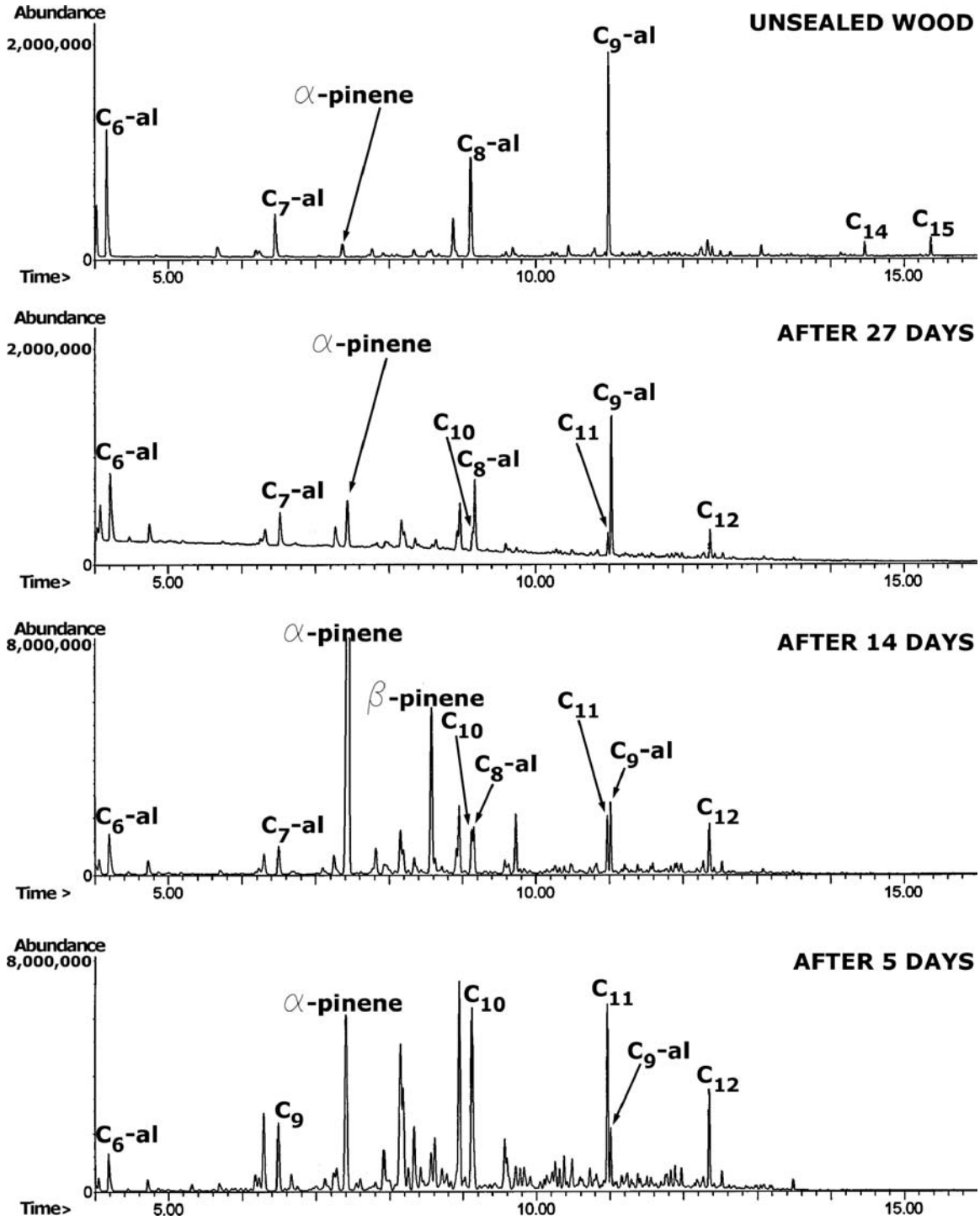

FIG. 4—*The total ion chromatograms obtained in the MPD range from the passive headspace analysis of the 18 cm board lengths after the number of days noted. The straight chain hydrocarbons are noted by the letter "C" and the number of carbons in the chain (e.g., decane is represented by "C_{10}"). The straight chain aldehydes are indicated by the number of carbons in the chain followed by "-al" (e.g., hexanal is represented by C_6-al).*

covered approximately 27% of the daylight hours. The overall average outdoor temperature over this 27-day period was 19°C (67°F) with a maximum of 31°C (87°F) and a minimum of 7°C (45°F) (9).

Conclusion

While the ignitable liquid of interior floor coatings has been reported to persist for 2 years (3), this study showed the amount of time an ignitable liquid remains in exterior wood sealed with chemical treatment containing MPD is considerably shorter, less than 1 month. This is possibly due to the differences in the type of coating the product used produced and/or the environment to which the wood was exposed. In some of the interior floor coating testing, a relatively impenetrable, unbreathable finish layer was placed on the wood, trapping the MPD within while exposing the wood to an indoor environment of "conditioned" air. In contrast, the finish layer

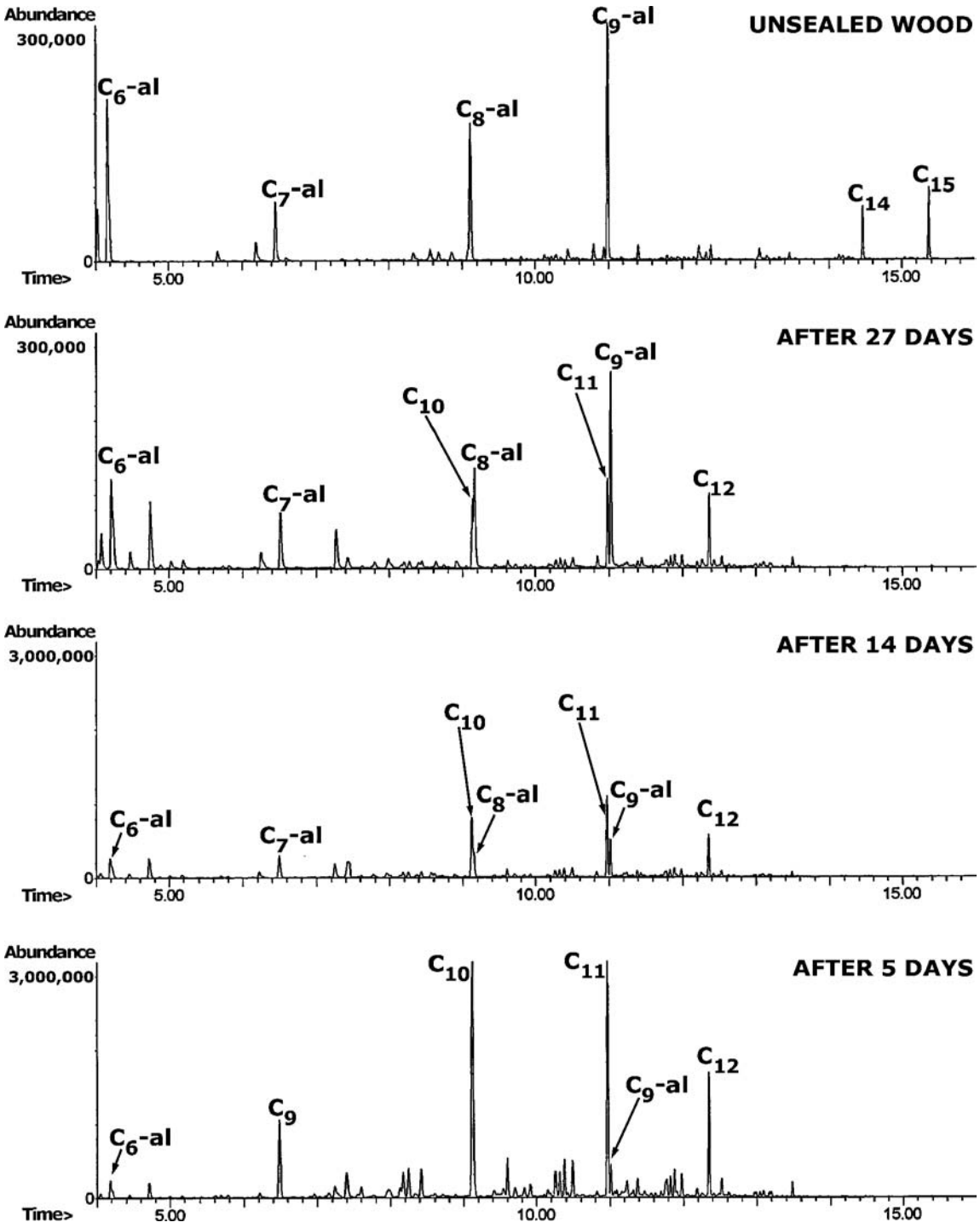

FIG. 5—*The alkane mass chromatograms (sum of ions 43, 57, 71, and 85) obtained in the MPD range from the passive headspace analysis of the 18 cm board lengths after the number of days noted. The straight chain hydrocarbons are noted by the letter "C" and the number of carbons in the chain (e.g. decane is represented by "C_{10}"). The straight chain aldehydes are indicated by the number of carbons in the chain followed by "-al" (e.g., hexanal is represented by C_6-al).*

placed on the exterior wood in this study consisted of a relatively soft wax while the wood was exposed to outdoor temperature and humidity extremes.

In this test, a medium petroleum distillate was isolated on a Thompson's WaterSeal® treated board up to 16 days after application, but not 20 days after application and with exposure to the outdoors. As the test was conducted in relatively sunny and warm conditions, one could expect the medium petroleum distillate to be isolated from a sealed board after a longer interval when the outdoor temperatures are cooler. [Further testing in cooler weather should be investigated to verify this hypothesis]. Comparison samples are imperative. A comparison sample of the matrix taken away from the origin area (e.g., decking from the opposite side of the deck), and/or a comparison sample of the

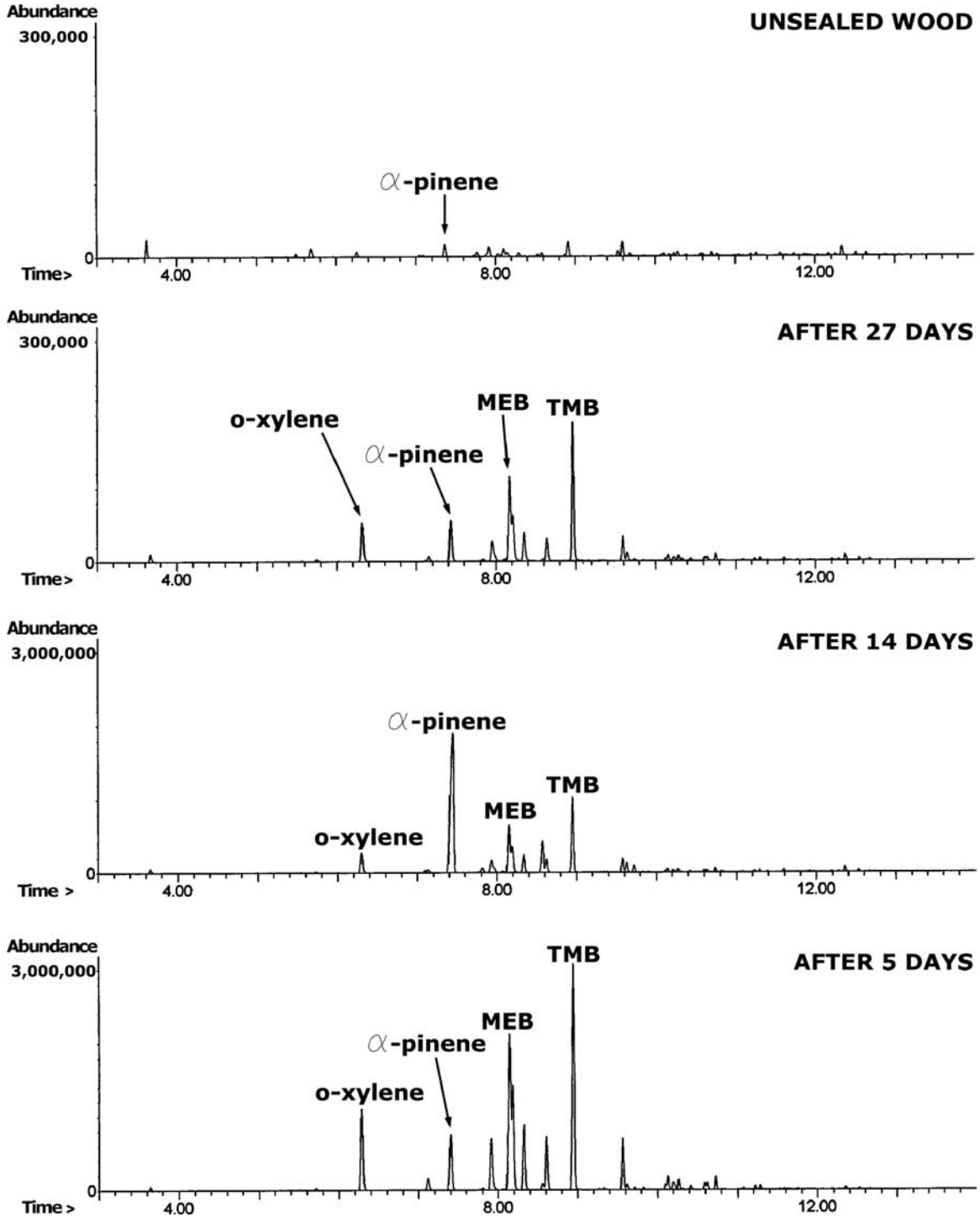

FIG. 6—*The aromatic mass chromatograms (sum of ions 91, 105, and 119) obtained in the MPD range from the passive headspace analysis of the 18 cm board lengths after the number of days noted. "MEB" denotes 1-methyl-2-ethylbenzene while "TMB" denotes 1,2,4-trimethylbenzene.*

product used to "seal" the matrix may help to determine if any ignitable residue isolated on a sample of a sealed product was indeed foreign.

Interpretation of the data gathered by the analyst must be complete as the treated wood used in this test was found to have an aldehyde residue that, without mass spectrometry detection and further investigation, could be mistaken for normal hydrocarbons encompassing the C7 to C11 range. The analyst must also be aware that residues obtained using passive headspace analysis can be biased against heavier components so a wax or mineral oil type product can resemble a heavy petroleum product (such as diesel fuel). In such a case, the analyst should take additional steps, such as solvent extraction, to identify the residue isolated.

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