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Analysis of Paraffin Wax in Fire Remains

Candles are sometimes used for arson because of fairly predictable delay in ignition of other combustibles as the candle burns down. Also, they are easily consumed in the resulting fire. It has been known that residues of paraffin often survive a fire and can be detected by chemical or physical means. Extraction procedures have usually been used to remove paraffin residues from fire remains. The isolated paraffin could then be characterized by infrared spectrophotometry, melting point, or X-ray pattern [1]. There are a number of other analytical procedures that have been used for paraffin wax, although not necessarily with regard to arson investigation. These include differential scanning calorimetry [2], differential thermal analysis [3], mass spectrometry [4], liquid-phase chromatography [5], and vapor-phase chromatography starting with Ogilvie et al [6]. Some of the methods are useful for distinguishing among samples of known waxes but do not give a detailed fingerprint of composition. Vapor-phase chromatography combines simplicity with the best yield of information on wax composition.

Paraffin wax is a mixture of straight-chain hydrocarbons ranging generally from about 20 to 40 carbon atoms per chain. The most common paraffin, which is used for home canning, candles, and other general use, is composed of hydrocarbons of about 21 to 33 carbon atoms. Paraffin waxes are often used in waterproofing compounds, polishes, lubricants, food wrapping, cosmetics, and many other products in small amounts. Thus, it is a ubiquitous substance and finding traces of it in burned materials is not in itself proof of arson by candle.

Hydrocarbons of paraffin wax would boil in a range from about 300° to about 500°C at atmospheric pressure. Above 400°C the hydrocarbons begin to pyrolyze and break down into smaller molecules or split out hydrogen. The boiling range of the paraffin components is sufficiently high and narrow that the wax which remains after a fire may be expected to have nearly the same composition as the original wax. Also, any unusual characteristics, such as higher molecular weight range or higher concentration of certain components, may be expected to be recognizable by analysis of the wax in the fire remains. Vapor-phase chromatography was selected as the means to best show these characteristics.

Experimental

Several experiments were conducted to show the possibilities of analyzing wax

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residues. In the first experiment, corrugated paper, pine veneer, paper towel, sawdust, and cheesecloth were arranged in a stack. A 5.0-g lump of paraffin wax (melting point 55 to 56°C) was placed on the center of the stack. Several such stacks were ignited with matches and allowed to burn for various lengths of time. Fire was extinguished with a small stream of water and the remains were allowed to cool. The material was transferred to a beaker and 100 ml of chloroform were added. The beaker was warmed for 20 min and the chloroform was decanted and filtered. Another 50 ml of chloroform were added, allowed to stand warm for 20 min, and then decanted and filtered. The combined filtrates were dried to give the crude wax extract.

The above procedure was repeated using crayon and again using beeswax in place of paraffin. A separate experiment showed that paraffin is consumed nearly linearly with the consumption of the substrate, sawdust.

Crude wax extracts or other wax products were prepared for analysis by dissolving the product in hexane (or heptane) and decanting the solution at room temperature from any insoluble residue. The hexane solution was passed through a column (7 by 60 to 80 mm) of activated alumina (Fisher Scientific, 80–200 mesh) without additional treatment. The eluate was allowed to evaporate to dryness, giving a waxy residue consisting of aliphatic hydrocarbons [7].

Gas chromatography was used to characterize the purified waxes. The instrument was an F&M Model 609 with a flame ionization detector. A 1.5-m by 3.2-mm column of SE-30 silicone rubber at 10% loading on Chromosorb P (60–80 mesh, acid washed) was used. The temperature was programmed from 175°C to rise at 9°C/min to 320°C and then hold constant. When polymeric waxes or other residues of low volatility accumulated on the column, they were removed by holding the column above 300°C with carrier gas flowing. There was no noticeable deterioration of column performance.

Portions of the wax extracts were dissolved in carbon disulfide at 10 mg/ml⁻¹ and a 10- μ l portion was injected into the sample port. The elution times were usually checked with an internal standard consisting of a trace of hexadecane in the carbon disulfide.

The above procedure was used to analyze ten different candles, three brands of crayon, six floor waxes, a furniture wax, "hard" paraffin wax, "soft" paraffin wax, beeswax, carnauba wax, chewing gum, Glow Globbs®, cheese wrapping, Parafilm®, shoe polish, and waxed paper.

Results

The gas chromatograms were generally as shown for hard paraffin in Fig. 1. Resolution was good enough to nearly separate each peak. There was a sharp rise in the baseline as the temperature rose above 250°C. This baseline shift could be eliminated with proper changes in operating parameters, but did not cause any particular difficulty in analyzing the waxes. Because of the lack of automatic integrating devices, individual peaks were measured for height above the adjusted baseline, which is shown as a dashed line. The validity of the adjusted baseline was confirmed by a run with pure carbon disulfide, which gave a curve of that shape.

In these experiments the extracts were normally purified with a column of activated alumina. Where large amounts of wax are involved, the purification is unnecessary for gas chromatographic analysis. Where small amounts and traces of wax are extracted, the purification is desirable for gas chromatography and necessary for infrared spectrophotometry.

Peak heights were measured in centimetres, totalled, and then each peak was divided

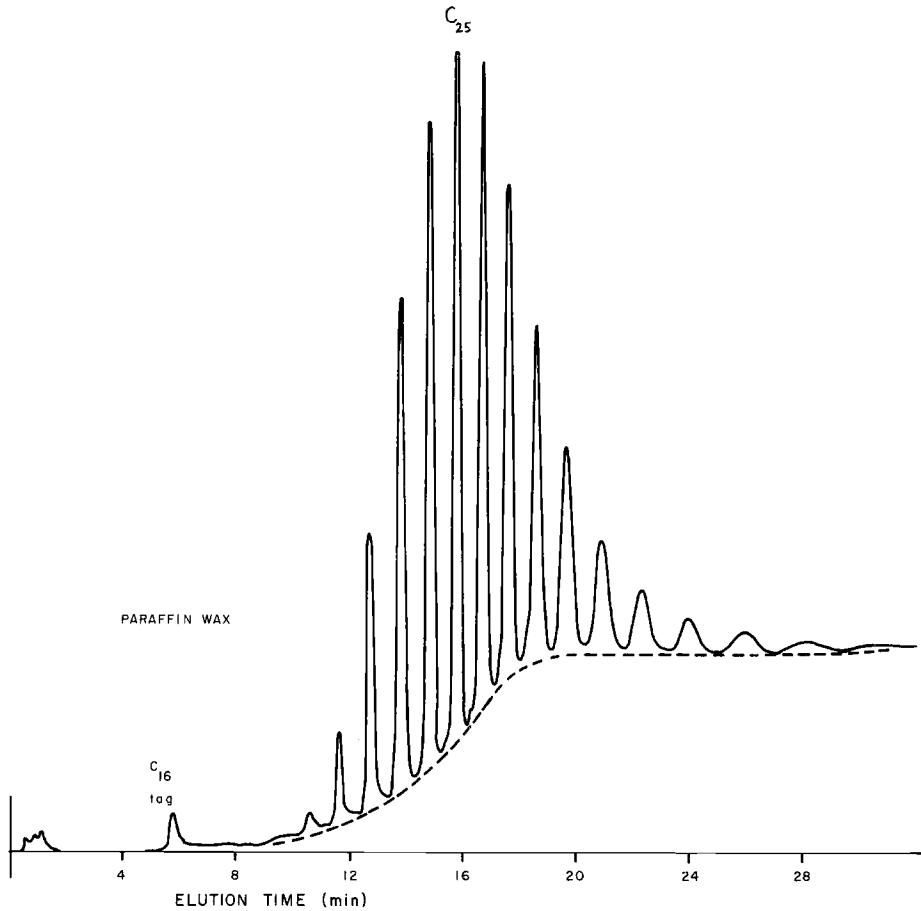


FIG. 1—Gas chromatogram of paraffin wax.

by the total. This gave an apparent percentage composition. In a few cases peak areas were calculated from peak height times width at half height. Areas were totalled and each peak divided by the total. The general picture did not change compared to, the picture from peak heights, but percentages of the last eluting components doubled (because of the wide peaks), whereas the percentages of the first peaks were less. The middle peaks with the highest percentages did not change much.

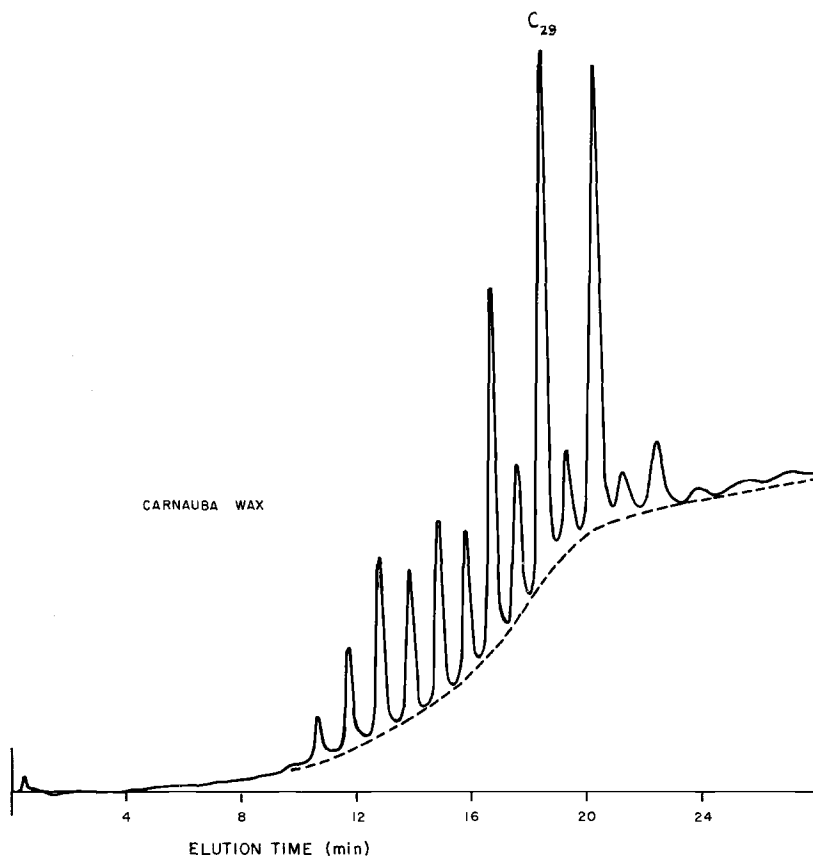
Table 1 shows the results from the experiment in which paraffin wax was burned for various lengths of time. Recovery was 87% when no paraffin was burned. There was no attempt to make the extractions quantitative because, at this state of the art, quantitative relations of hydrocarbons to char have questionable significance. Even when nearly completely consumed, the characteristics of the paraffin wax remained nearly constant. A trace of wax with the same characteristics as hard paraffin was found in the bare unburned substrates (last line).

The same experiment with beeswax and crayon showed the persistence of distinguishing characteristics when those waxes were recovered from the char at 16 and 4%, respectively.

TABLE 1—*Effects of burning on composition of wax.*

Burning Time, min	Wax at Start, g	Wax at End, g	Recovery, %	Carbon Number Range	Carbon Number Maximum
0	5.0	4.36	87	C ₂₁ –C ₃₁	C ₂₅
2	5.0	3.66	73	C ₂₁ –C ₃₁	C ₂₅
4	5.0	1.70	34	C ₂₁ –C ₃₁	C ₂₅
6	5.0	0.73	15	C ₂₁ –C ₃₁	C ₂₅
8	5.0	0.22	4	C ₂₁ –C ₃₁	C ₂₅
9	5.0	0.01	0.2	C ₂₁ –C ₃₁	C ₂₅
3.5	0	0.01	...	C ₂₁ –C ₃₁	C ₂₅

Figure 2 shows a chromatogram of the hydrocarbons which were isolated from carnauba wax by the previously described procedure. The bulk of the natural wax consists of esters of long-chain acids and alcohols plus free acids and other miscellaneous compounds. All but hydrocarbons are retained by activated alumina when eluted with hexane.

FIG. 2—*Gas chromatogram of hydrocarbons from carnauba wax.*

Aliphatic hydrocarbons from natural sources contain a predominance of odd-numbered carbon chains. This results from decarboxylation of the natural, even-numbered acids built up from acetyl units. Each natural wax has its own characteristic pattern of hydrocarbons.

If the chromatogram of paraffin wax is adjusted to give a flat baseline, a smooth, nearly Gaussian curve could be drawn through the tops of the peaks. This is obviously not possible with the chromatogram of carnauba hydrocarbons. The apparent percentages can be plotted to give a smooth curve for paraffin (Fig. 3). Because of the petroleum origin of paraffin wax and the preparation of the wax by distillation, there is a normal distribution of molecule sizes around a middle value. (The curved line connecting each point has no intrinsic significance but merely serves to more clearly illustrate the pattern.)

If a smooth curve is drawn through the even-numbered components of carnauba hydrocarbons, the odd-numbered ones stand out in excess (Fig. 3). The curve is smooth but not Gaussian. This points out a way of distinguishing waxes by their general pattern of distribution, range, and predominant components. Figure 3 also shows the distribution of hydrocarbons from a floor wax (Trewax®). There is a large proportion of the wax above C₃₂. Also, the odd-numbered components are in excess of the general curve. Either characteristic would distinguish this residue from the residues from any of the candles analyzed. Hildebrand et al [8] found a smooth distribution of wax from petroleum and odd-even discrepancies in wax from lignite.

Figure 4 shows the results of the experiment in which crayon or beeswax was burned and the residue analyzed. The dashed lines are for the hydrocarbons as isolated from the whole unburned substances. The solid lines show the values for similar analyses after being mostly consumed in a fire. One is shown with a drawn envelope and the other as a bar graph. There is a noticeable decrease in the lower molecular weight components in both cases. This shows that there is some tendency for the more volatile components to be lost preferentially; however, the distinguishing characteristics of each wax remain. The crayon (Crayola) contains higher molecular weight hydrocarbons (C₂₄ to C₃₅, with the maximum at C₂₉) than common hard paraffin wax. It also contains some natural wax, as the odd-numbered components make bumps in the curves. Two other brands of crayon gave chromatograms very similar to that of hard paraffin.

Figure 5 shows hydrocarbon extracts from several products, giving a variety of shapes, ranges, and distributions. Unfortunately, most candles are close to the curve for the candle shown, which is essentially identical to the hard paraffin wax shown earlier. There were some shifts in range of carbon numbers and carbon number of the predominant component (maximum of the curve), amounting to one or two carbon numbers. The shoe polish (Kiwi) contains some natural wax as shown by the bumps at C₂₉ and C₃₁. A good-quality dipped candle had a coating of soft wax at the base to allow it to be pressed into a holder. Analysis showed that the soft wax had a range from C₂₀ to C₃₂, with the maximum at C₂₄. The rest of the candle ranged from C₂₁ to C₃₁, with a maximum at C₂₅.

This work points out the need for caution in attributing paraffin wax, extracted from fire evidence, to a candle. At the same time it points out that if there are any distinguishing characteristics of the hydrocarbons in the wax, these can be determined fairly easily. Thus, the source of the wax may be more accurately identified. With more modern instruments, including digital integration and computer tie-in, this kind of analysis can be performed even faster and more accurately.

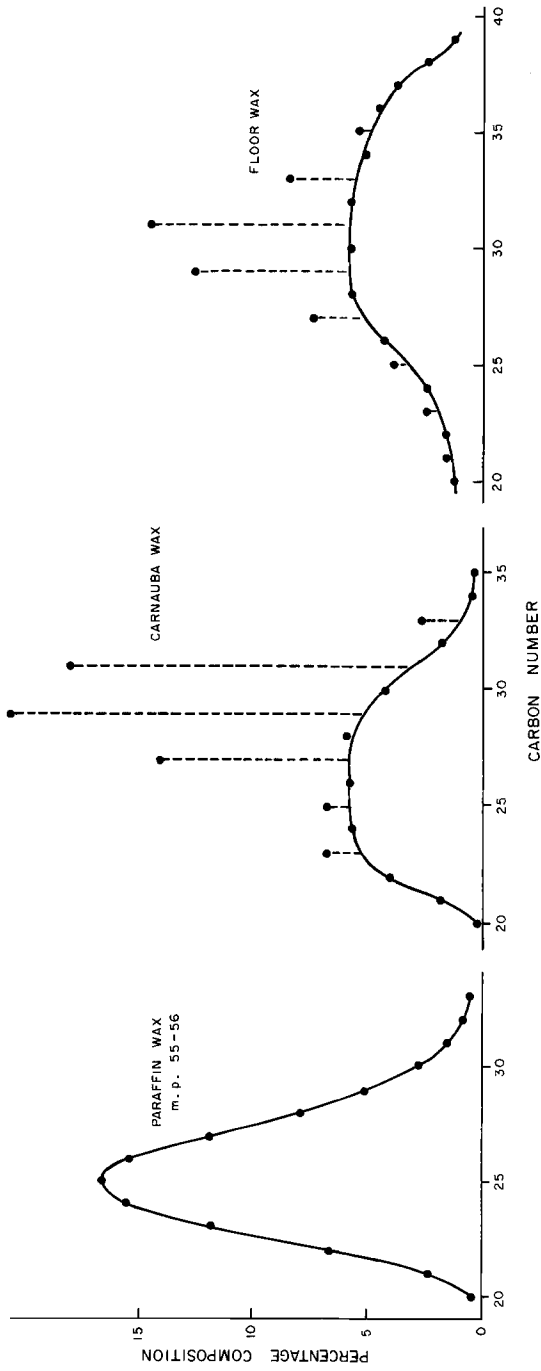


FIG. 3—Composition of paraffin wax and hydrocarbons from carnauba wax and a floor wax.

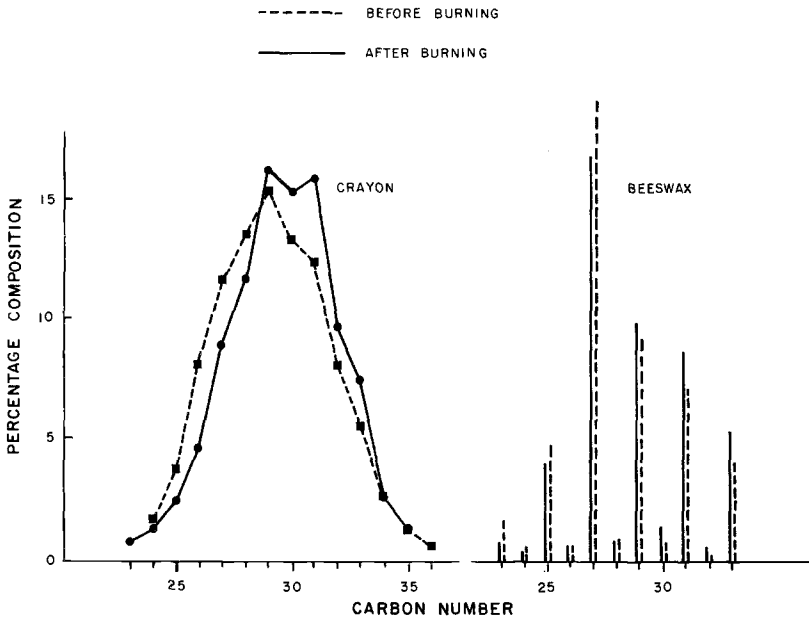


FIG. 4—Composition of hydrocarbons from a crayon and from beeswax before and after burning.

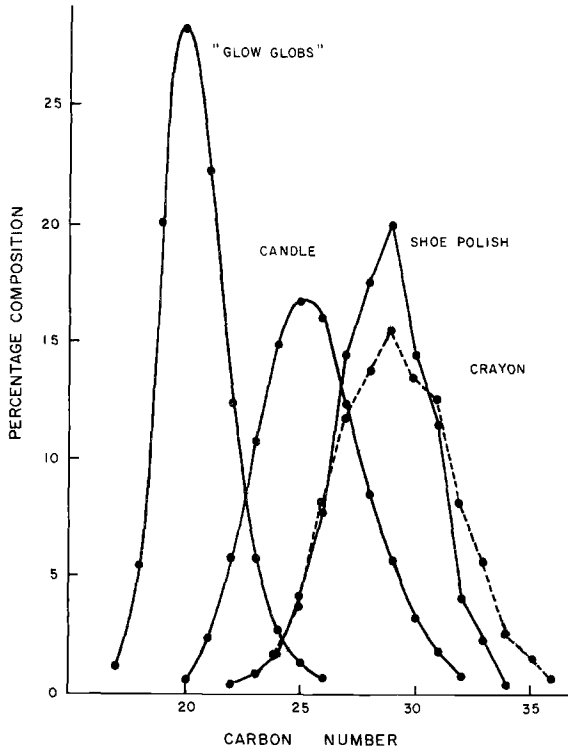


FIG. 5—Composition of hydrocarbons from several common products.

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