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SEPARATION OF FLAMMABLE MATERIAL OF PETROLEUM ORIGIN FROM EVIDENCE SUBMITTED IN CASES INVOLVING FIRES AND SUSPECTED ARSON

J. W. BRACKETT, JR.

J. W. Brackett, Jr. is a member of the staff of the Laboratory of Criminalistics, Office of the District Attorney, San Jose, California, and has previously contributed to this Journal. The material discussed in this article has been presented at the November, 1954, meeting of the California Association of Criminalists, and subsequently at the Criminalistic Section meeting of the American Academy of Forensic Sciences. Mr. Brackett is a member of California Association of Criminalists.—EDITOR.

Evidence is often submitted in cases involving fires, especially in arson investigations, for the purpose of demonstrating the presence or absence of flammable substances which may have been added to accelerate the spread of the fire. The usual accelerant is a petroleum product such as kerosene, gasoline, or oil; and if present, is submitted for analysis in the presence of a large excess of extraneous scorched and burned material, often soaked with water. The first step of the laboratory investigation is usually an operation to separate any accelerants which may be present from the evidence.

Methods which have been used in this separation are immiscible phase flotation, simple distillation, steam distillation, vacuum distillation, and extraction procedures. Immiscible phase flotation, which consists in flooding the evidence with water and recovering the lighter-than-water, water insoluble phase, requires a high concentration of accelerant, and even then the recoveries are poor. Simple distillation procedures are satisfactory only when low boiling accelerants are used (2). The vacuum distillation process (1, 3) is time-consuming, requires expensive vacuum apparatus, refrigerants which are difficult to store, and yields a product which is separated into fractions which may be difficult to identify with the original accelerant. Extraction procedures do not separate volatile materials in good yield. Steam distillation is rapid, requires a minimum of simple apparatus and technique but gives acceptable yields only with easily volatile substances such as gasoline.

It was proposed to adapt the reflux type distillation trap such as used in ASTM Test D-322 to effect the separation by steam distillation and to increase the speed and efficiency of the process by choice of suitable immiscible carrier liquids and optimum operating conditions. As a result of this study, experimental recoveries of over 90% of gasolines, solvents, and kerosenes were obtained in one hour.

The principal of steam distillation is that two immiscible liquids exert their own vapor pressures independently of each other. The total pressure is the sum of the two vapor pressures at the temperature concerned. When the sum of the two vapor pressures is equal to the surrounding pressure, the liquids will boil. Thus, it is possible to vaporize a substance in the presence of a suitable volatile immiscible carrier liquid, transfer the vapors to a condenser, condense the vapor, separate the two liquids, and recover the less volatile substance continuously by use of a temperature well below its boiling point.

The mole ratio of a substance in the vapor is equal to the ratio of its vapor pressure to the total pressure of the distillation. Using the equation of Clausius and Clapeyron with its simplifying assumptions, an expression can be derived to compute the equilibrium molal ratio of the vapors of a given pair of pure immiscible liquids and at a known operating temperature. Because of phase rule, when there is excess liquid carrier present in the boiler the operating temperature may be varied at will by increasing or decreasing the pressure of the system.

$$\frac{M_p}{M_p + M_c} = \frac{1}{1 + \text{antilog} \frac{1}{2.3R} \left(\frac{L_1}{T_c} - \frac{L_2}{T_p} + \frac{L_2 - L_1}{T} \right)}$$

In this equation

$$\begin{aligned} \frac{M_p}{M_p + M_c} &= \text{molal ratio of product material in vapor (and hence condensate phase)} \\ &= \frac{\text{moles of product}}{\text{moles of product} + \text{moles of carrier}} \end{aligned}$$

It is evident that as this ratio is increased, the efficiency of the process is increased.

The variables in the denominator on the right hand side of the equation are:

L_1 Latent heat of vaporization of the carrier liquid, calories per mole

T_c Absolute boiling temperature of the carrier liquid at atmospheric pressure

L_2 Latent heat of vaporization of product (less volatile) liquid, calories per mole

T_p Absolute boiling temperature of the product (less volatile) liquid at atmospheric pressure

T Absolute operating temperature which, in a univariant system depends on the pressure, T_c and T_p

R Gas constant 1.99 calories per mole

This equation has not been tested experimentally, but qualitative agreement is indicated by experimental data to be presented shortly.

On observing the equation it is apparent that the mole ratio of the less volatile substance is increased by increasing boiling point of carrier liquid, and if the latent heat of vaporization of the more volatile liquid is greater than that of the less volatile liquid, the mole ratio is increased by decreasing temperature of operation.

A more elaborate equation is available to fit the practical case; that is, where the latent heat of vaporization and composition vary continuously during the distillation process. This new equation has not been tested experimentally, but the effect of changing the operating conditions is qualitatively the same as the equation shown previously.

The extent of attainment of equilibrium cannot be predicted although it would seem that true equilibrium would be reached faster by increasing the temperature. It is obvious that the amount of product in the still decreases as a result of the distillation process and the overall efficiency will decrease to zero.

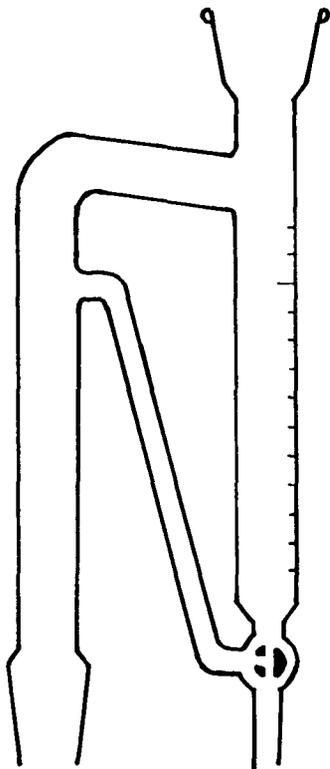


Figure 1

A perfected design of ASTM D-322 trap which is somewhat more efficient than that shown in Figure 2.

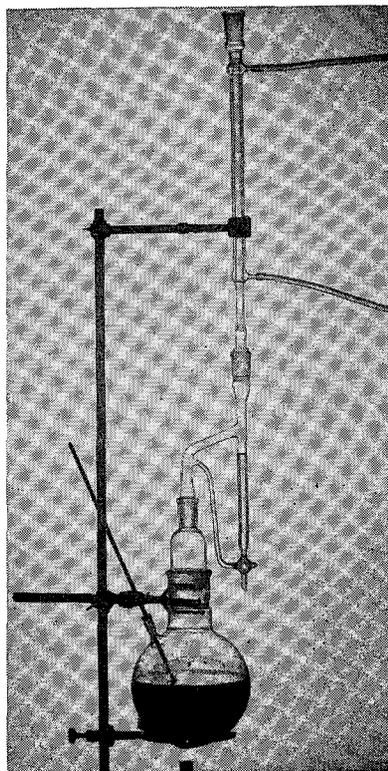


Figure 2

Assembled Apparatus

A practical limitation is that the temperature of operation must not be too great otherwise the product will be altered or thermally decomposed or interfering material may distill from the extraneous part of the evidence.

Desirable characteristics of a carrier liquid can now be defined. It must be mutually insoluble with possible products. It must boil as high as practicable. Its latent heat of vaporization must be as small as possible.

Water, ethylene glycol and its homologues, and glycerol were picked as carrier liquids. Simple tests indicated that ethylene glycol and glycerol were relatively insoluble in typical petroleum products.

APPARATUS

Flask, round bottom, Pyrex, 2 liter capacity, fitted with female ground glass ST joint 55/50. This size joint will admit most evidence usually encountered; e.g., rags, ashes, excelsior, etc. A side opening female ST joint 10/30 may be added if use of thermometer, external steam, or vacuum is contemplated.

A larger vessel could be used as a boiler if required.

Adapter, Pyrex, top joint ground glass female ST joint 24/40, bottom joint ST 55/50 male. Overall height should not exceed 6".

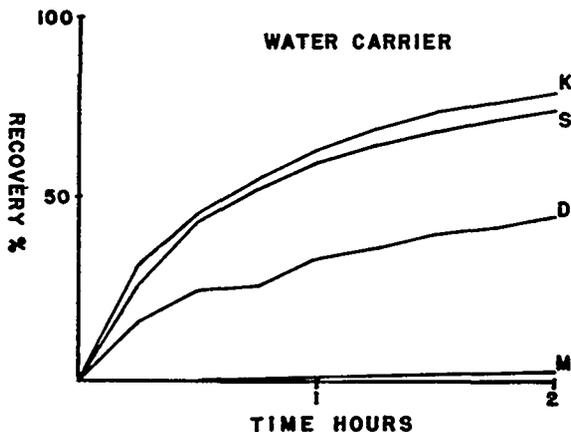


Figure 3

Vertical scale shows the amount of product recovered; the horizontal scale, the elapsed time. The zero of time is when the first condensate hits the trap. K indicates Kerosene; S, Stove Oil; D, Diesel Fuel; and M, SAE 10 Motor Oil.

Trap, reflux, modified ASTM D-322¹, bottom (vapor inlet) joint ground glass male ST 24/40; top (condensate return to graduated portion of the trap) joint ground glass female, size as required by condenser. Should ASTM D-322 trap be modified, for best results the indent above the graduation should be removed, the vapor inlet tube reversed in slope, and a three-way ST glass stopcock inserted as shown in figure 1.

Condenser, Liebig or equivalent, with suitable length, with ground glass male joint as required by top joint of trap.

Ring Stand, Clamps, Heat Source, available from laboratory supplies.

REAGENTS

Distilled water.

Ethylene glycol, BP 197°C, Central Scientific Company C1965.

Glycerol USP BP 290°C.

Phosphorus pentoxide—sulfuric acid reagent—a solution of 300 grams of phosphorus pentoxide in 700 grams of 96% sulfuric acid.

Petroleum products, obtained from Standard Oil Company of California, San Jose Sales Office.

PROCEDURE

The evidence is put into the flask, and carrier liquid is added until two-thirds full. If a low boiling accelerant is suspected, water is the proper carrier, otherwise ethylene glycol is used. The flask, adapter, trap and condenser are connected as shown in figure 2. Necessary condenser cooling arrangements are made. Heat is applied to the bottom of the flask to provide a gentle boil. The trap is designed to return the condensed carrier liquid to the flask, retaining the lighter immiscible accelerant. The trap should be observed occasionally during operation to insure that it is cool enough to retain the product. For very volatile material, additional local cooling of the trap may be necessary. The process is continued

¹ Available from Microchemical Specialities Company, 1834 University Avenue, Berkeley, California.

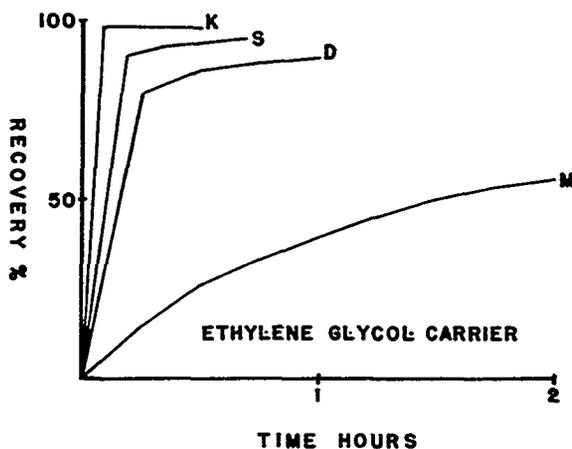


Figure 4

The scales and symbols are the same as in Figure 3.

until the volume of the retained layer becomes constant. Should the trap fill with a retained layer, it may be removed by stopcock, taking care to extinguish all open flames in the vicinity. The product, if any, is subjected to purification and identification tests as required to suit the purpose of the investigation.

RESULTS

Comparative time recovery curves are shown for the common petroleum products encountered. Figure 3 shows the results with water as a carrier; figure 4 with ethylene glycol. The increase in speed of process, and increased recoveries caused by higher operating temperatures is evident.

In these test runs, 10 ml of petroleum product was added to 30 grams of surgical cotton in the flask; 1 liter of carrier was added. Tap water, temperature 16°C was used as the only coolant. Aside from shielding the trap from hot air of burner with asbestos shield, no additional cooling was used. The zero of time was taken when the first drop of condensate hit the trap. The determinations were arbitrarily stopped when less than .1 ml of product was recovered in 15 minutes. No corrections were made for solubility of products in carrier, nor for volatility of products. The recovered products were cooled to room temperature before the final recovery volumes were measured. The operating recovery volumes were estimated using .9 of the measured volume at the temperature of the test.

Table I shows the materials, recoveries, refractive indices, carrier used, and time of test.

A test was made using glycerol, boiling point 290° C, as a carrier liquid using SAE 40 oil as the product tested. Extensive cracking resulted, and the product was different in physical properties from the parent material. Further high temperature tests were abandoned.

Reduced pressure water carrier distillations were tested at a pressure of 30 cm Hg which corresponds to 75° C operating temperature. Lower temperatures and lower pressures caused operational difficulties without special equipment. Although the

TABLE I

| Product | Mfgr Boiling Range of | R.I. 25°C | Water Carrier | | | Ethylene Glycol Carrier | | |
|--------------------------------------|-----------------------|-----------|---------------|----------|--------------|-------------------------|----------|--------------|
| | | | Recov-ery % | Time Hrs | R.I. Product | Recov-ery % | Time Hrs | R.I. Product |
| White gasoline..... | 112-244 | 1.399 | 77 | ¾ | 1.405 | | | |
| Regular gasoline..... | | 1.419 | 71 | 2 | 1.434 | | | |
| Premium gasoline..... | | 1.416 | 71 | ½ | 1.434 | 71 | ½ | 1.429 |
| Stoddard solvent..... | 350 | 1.428 | 98 | 1 | 1.429 | | | |
| Kerosene..... | 358-524 | 1.442 | 89 | 4.5 | 1.442 | 98 | ½ | 1.442 |
| Stove oil..... | 350-576 | 1.464 | 81 | 3.5 | 1.464 | 96 | 1 | 1.463 |
| Diesel fuel..... | 386-686 | 1.481 | 58 | 5 | 1.480 | 90 | 1 | 1.471 |
| SAE 10 motor oil..... | | 1.480 | 3 | 2 | Not Det. | 60 | 3½ | 1.476 |
| "Topped" premium gaso- oline..... | | 1.438 | | | | 90 | 1 | 1.438 |

initial rates of recovery using kerosene were higher, the rates of recovery decreased rapidly and the overall yields were smaller than those obtained by use of water at atmospheric pressure. Inasmuch as it is possible to obtain the advantages of lower operating temperatures by simpler means, no further experiments with reduced pressures were made.

DISCUSSION

Low boiling petroleum products such as gasoline showed differences in physical properties before and after recovery with use of both water and ethylene glycol carriers. Low recoveries also resulted. Provisions made for increasing the condenser cooling capacity and cooling the retainment trap caused little or no improvement. These low yields and changes in physical properties were shown to be caused by evaporation of lighter components while the sample was added to the boiling flask. Nearly complete recoveries of the same gasoline with little change in R.I. were obtained on allowing the more volatile components to evaporate off for a short time before a test was made.

Approximately 25 ml of premium grade gasoline, R.I. 1.416, were allowed to stand in a 9 cm diameter petri dish with slight stirring. The R.I. changed rapidly and when it reached a value 1.438 (approximately 10 minutes) a sample was taken and added to flask with 30 gms of cotton for test.

Results: Ethylene Glycol Carrier

R.I. added 1.438, R.I. recovered 1.438

Recovery—90% See Table I, "Topped Gasoline"

The same gasoline was used as test material without previous evaporation of the more volatile components.

Results: Ethylene Glycol Carrier

R.I. added 1.416, R.I. recovered 1.429

Recovery—71% See Table I, "Premium Gasoline"

Inasmuch as evaporation of low boiling components would have occurred in a practical case, no further work was done to improve these yields.

Composition changes such as cracking or fractionation are insignificant using

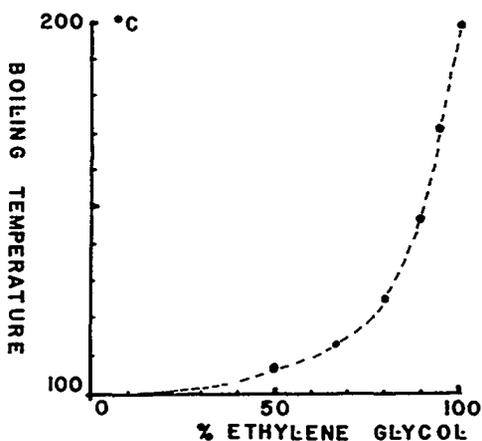


Figure 5

The vertical scale shows equilibrium boiling point in degrees centigrade; the horizontal scale percentage ethylene glycol in boiling mixture. The remainder of the boiling mixture is water. The values shown are for the apparatus illustrated at atmospheric pressure.

either water or ethylene glycol as carrier liquid as shown by comparison of refractive indices of added material and product recovered.

To determine if appreciable amounts of common evidence material would produce interferences, blank runs without added petroleum products were made on cotton cloth, Douglas fir, sugar pine, redwood, and butyl rubber. Water was used as a carrier in these tests. 100 grams of each substance was tested. Cotton and redwood yielded less than .1% of immiscible oil. The Douglas fir and sugar pine produced about .2% of a volatile oil which could be readily differentiated from any petroleum accelerant as it was much higher in refractive index and had a distinctive odor. The butyl rubber produced .1% of a volatile oil which could not be readily distinguished from the higher boiling petroleum products by refractive index alone, but which disappeared on sulfonation with the $P_2O_5-H_2SO_4$ reagent, hence was different from the other petroleum products tested.

Blank tests without added petroleum products were then made using ethylene glycol as a carrier. The same substances and amounts were used as with water in the paragraph above. Cotton, Douglas fir, sugar pine, and redwood gave the same blanks as with water. Butyl rubber, however, gave 3% of a volatile material in two hours which was of about the same refractive index as the high boiling petroleum products and which was not completely destroyed by sulfonation with the $P_2O_5-H_2SO_4$ reagent. This might be mistaken for an accelerant unless it is accounted for in a conclusion. It is possible that other materials such as paint, plastics, and saponifiable greases and oils may give high blanks.

Because the water and ethylene glycol can be separated by distillation and the reflux method of distillation is used, any mixture of ethylene glycol and water will soon reach an equilibrium boiling point. This temperature is that at which the amount of water lost by vaporization from the boiler is equal to the amount of water

returned in the reflux from the trap. Thus, any desired operating temperature between 100°–197° C may be obtained by removing distillate from the system through the trap until the desired operating temperature is reached. Then the temperature is stabilized by turning the stopcock to return reflux to the boiler. Composition-equilibrium boiling point data for this apparatus is shown in figure 5.

The recovered product, after washing with water, warm concentrated NaOH, and finally the $P_2O_5-H_2SO_4$ reagent, is compared with submitted reference material. The refined product is tested for flammability, and its specific gravity and R.I. are determined. Proper matching of properties makes possible the conclusion that a petroleum material similar to the comparison liquid was extracted from the evidence submitted.

SUMMARY

A method is presented for separating volatile petroleum products from evidence in cases involving fires by use of ethylene glycol as a carrier liquid in place of water in an ordinary steam distillation. As compared with vacuum distillation, less apparatus is required, time is saved, and more complete recoveries are obtained.

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