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Identification of Arson Accelerants by Gas Chromatographic Patterns Produced by a Digital Log Electrometer

The identification and comparison of accelerants is a problem which confronts the criminalist during the examination of evidence from suspected arson cases. The most common accelerants encountered in the investigation of arson are liquid hydrocarbons. The identification of these materials is complicated by the fact that they are not single chemical entities but complex mixtures of hundreds of different hydrocarbons.

A number of published articles have dealt with investigation, recovery, and identification of accelerants. Laboratory aspects of the investigation of arson cases were discussed [1,2] as well as recovery methods, which include vacuum distillation [3,4], steam distillation [5], air flushing [6], and solvent extraction [7-9]. Methods of identification were based on such properties as odor, boiling range, density, refractive index, and flash point [4]. Other methods of identification include absorption on paper and fluorescence [10,11] and infrared spectrophotometry [6,7].

With the advent of gas chromatography numerous articles have appeared which propose specific identification of the type of accelerants employed based on differences resulting from variations in the manufacturing process. These articles deal with use of the thermoconductivity detector [12-16] and the hydrogen flame detector [9,17,18] in characterizing the effluent from the column of the gas chromatograph and the amplification of the signal by a linear electrometer.

Electronic capabilities have progressed to the point where instruments are now commercially available which display chromatographic data in logarithmic form [19]. This paper will discuss the advantages of the digital log electrometer over the conventional linear electrometer.

Digital Log Electrometer

Wide current variations experienced in gas chromatography detectors frequently cause the loss of pertinent information. This condition is most noticeable with wide range detectors, such as of the flame ionization type, when small current peaks occurring close to large current peaks are obscured. This problem does not occur, however, when information is presented in logarithmic form covering three decades or more.

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Experimental results, obtained after analyzing a number of liquid mixtures with a gas chromatograph, indicate that logarithmic presentation of ion currents from a flame ionization detector is superior to linear presentation. The advantage is realized when mixtures are composed of components of widely differing concentrations. Since signal heights of 2 percent or less of full scale are barely detectable using linear electrometers, the range must be switched one or more times during a single analysis to detect all peaks or successive analyses must be made. Each succeeding analysis must employ greater sensitivity until all useful peaks are observed. The major disadvantage of the successive analysis method is that the experimental conditions cannot be exactly reproduced for each analysis and, thus, widely varying results may be obtained.

The minimum detectable signal height with a linear electrometer is about 2 percent of full scale. The minimum detectable signal with a four decade logarithmic electrometer is 0.01 percent of full scale. Thus, peaks up to one ten thousandth as high as the main peaks can be observed. The dynamic range of the electrometer is 10^{-11} to 10^{-7} A.

Figure 1 shows a sample of *n*-hexane with cyclohexane. The left side of the figure shows the *n*-hexane peak with only a small peak for cyclohexane for one set of conditions on a linear electrometer. The center of the figure shows a cyclohexane peak clearly; however, the *n*-hexane peak is off scale because of the change in attenuation of the linear electrometer required to make a clear presentation of the cyclohexane peak. The right side of the figure illustrates a single presentation of both peaks by the digital log electrometer. If other hexane isomers were present in the mixture, the center illustration would show the *n*-hexane peak to have a broader base. This could be misinterpreted as only one peak if the sample being analyzed were injected under one set of conditions only.

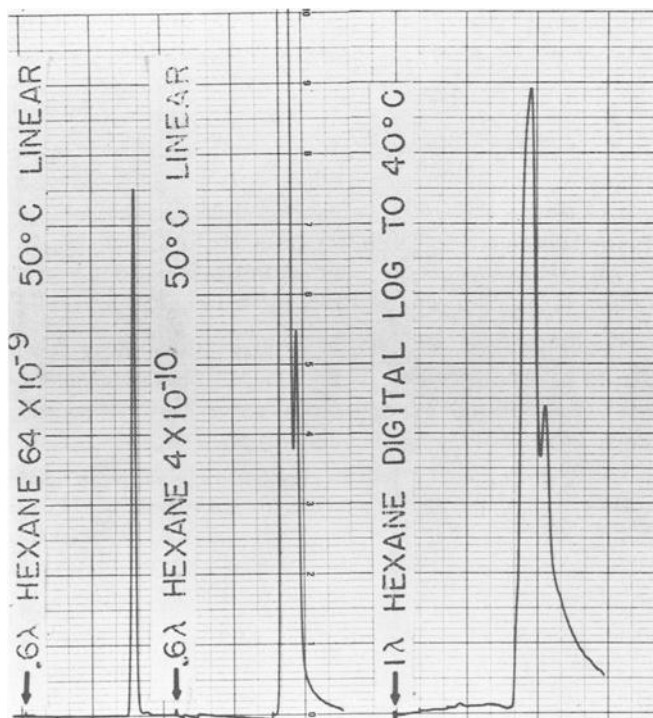


FIG. 1.—Comparison of linear electrometer and digital log electrometer presentation of *n*-hexane and cyclohexane analysis.

Experimental

Equipment

The gas chromatographic analyses were made with a Varian Model 1740-1 chromatograph with a hydrogen flame detector. This model is equipped with a temperature programmer. The linear presentations were made using the Varian electrometer. The digital log presentations were made with a Victoreen Model 4010-2 digital log electrometer fitted to work on the chromatograph. A Varian Model 20 recorder was used.

Operating Conditions

The following operating conditions were implemented.

Program 1—High boiling hydrocarbons.

Injection temperature: 225 C; oven temperature: isothermal at 40 C; programming begins at time of injection, continues at 2 deg C/min for 20 min, at which time the program is increased to 10 deg C/min, and ends at 250 C; detector temperature: 270 C. Carrier gas: helium—22 psi inlet pressure, 25 ml/min flow rate. Air—300 ml/min flow rate. Hydrogen—25 ml/min flow rate.

Column: 5 ft by $\frac{1}{8}$ in. SS; 3 percent SE 30 on 100/120 Varaport 30.

Sample size: 1 μ l.

Chart speed: 1 in./3 min.

Program 2—Low boiling hydrocarbons.

Injector temperature: 225 C; oven temperature: isothermal at 40 C for 6 min, after which it is programmed at 6 deg C/min to 225 C; detector temperature: 270 C.

Carrier gas: helium—30 psi inlet pressure, 15 ml/min flow rate. Air—300 ml/min flow rate. Hydrogen—25 ml/min flow rate.

Column: 15 ft by $\frac{1}{8}$ in. SS; 3 percent SE 30 on 100/120 Varaport 30.

Sample size: 1 μ l.

Chart speed: 1 in./3 min.

Program 3—Capillary column.

Injector temperature: 200 C; oven temperature: isothermal at 40 C for 6 min, after which it is programmed at 2 deg C/min to 125 C; detector temperature: 200 C.

Carrier gas: helium—35 psi inlet pressure; split, 2.5 ml/min flow rate; makeup, 22.5 ml/min flow rate. Air—250 ml/min flow rate. Hydrogen—25 ml/min flow rate.

Column: 200 ft by 0.01 in. inside diameter, SS, coated with Squalene.

Sample size: 1 μ l.

Chart speed: 1 in./3 min.

Materials

Standards: C₆ to C₁₆ paraffin hydrocarbons, Poly Science Qual-Kit No. 21.

Petroleum products: Full range of gasoline. Sixty-three specimens from Sacramento area collected in one day.

Procedure

To further illustrate the advantage of logarithmic display over linear display, a mixture of 10 paraffinic hydrocarbons, hexane through hexadecane minus pentadecane, was made up and injected into the gas chromatograph. Figure 2 illustrates the digital log electrometer display using a 1 μ l sample. Figure 3 illustrates a linear electrometer display using a 0.6 μ l sample. Both displays relate to samples run under the conditions of program 2. When only

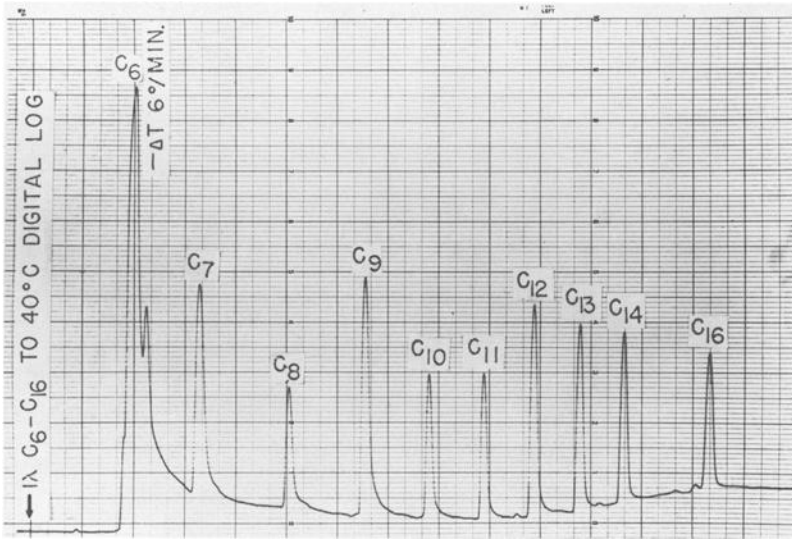


FIG. 2—Injection of mixture of C₆ to C₁₆ hydrocarbons.

a small peak resulted from hexane in Fig. 3, it was realized that a much greater attenuation was necessary to be able to present the other hydrocarbon peaks. The sample was temperature programmed and, because of the increased sensitivity necessary to record the other hydrocarbons in the sample, there was an increase in base line drift. The same hydrocarbon mixture was again analyzed by the same procedure only this time a 1.5 μl sample was injected. Figure 4 illustrates this presentation. Note that three attenuation changes

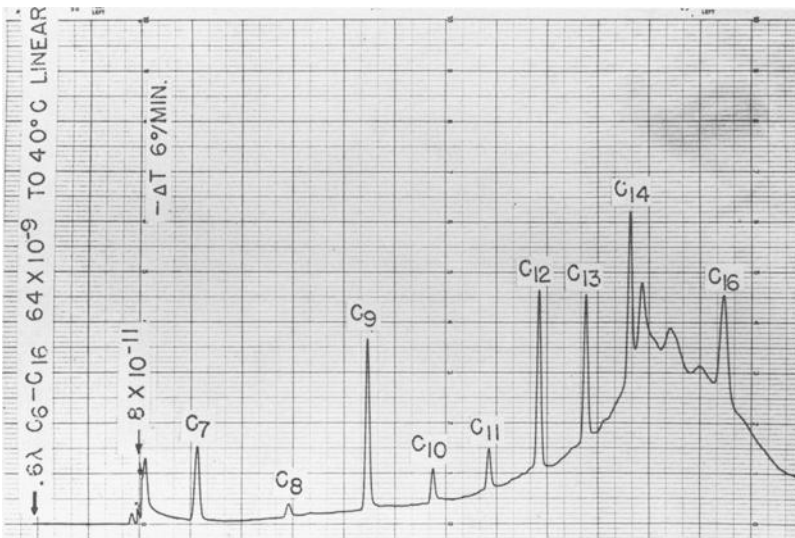


FIG. 3—Injection of mixture of C₆ to C₁₆ hydrocarbons.

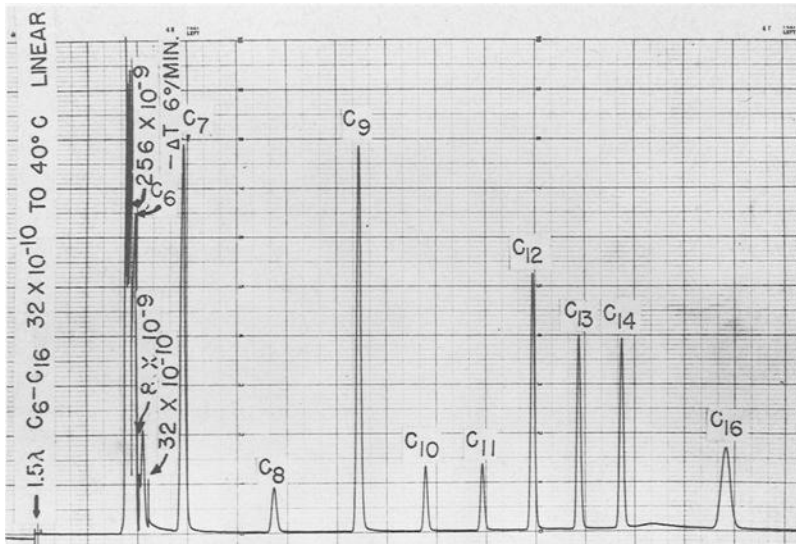


FIG. 4—1.5 μ l injection of mixture of C_6 to C_{16} hydrocarbons.

were required to keep all peaks on scale. Although Fig. 4 presents a classical textbook gas chromatographic chart from the C_7 through C_{16} hydrocarbons, several minor peaks are not present which are visible on the digital log presentation of Fig. 2 between C_{11} and C_{12} , between C_{13} and C_{14} , and before C_{16} .

To illustrate in yet another way the advantage of the digital log electrometer over the conventional linear electrometer, 1 μ l of Mohawk regular gasoline was mixed with 2.5 μ l of the mixture of C_6 to C_{16} paraffinic hydrocarbons used for the displays given in Figs. 2-4 and injected into the gas chromatograph. The linear display appears in Fig. 5 and the digital log display in Fig. 6. For comparison, Figs. 7 and 8 illustrate the same gasoline without the C_6 to C_{16} paraffinic hydrocarbons added. Note that not only can the peaks be identified by injecting an internal standard with the sample (aromatic and olefinic standards are also available) but also the increased sensitivities of some of the minor components are visible because of the greater dynamic range allowed by the digital log electrometer for one analysis of the sample. Figure 5 again illustrates the loss of one peak due to the unchanged attenuation, giving one broad peak for hexane. Program 2 conditions were used to obtain the displays in Figs. 5 through 8.

Logarithmic presentation of gas chromatographic data is superior to linear presentation because it has a greater dynamic scope and does not require range switching between decades. Since the electrometer operates on an integrating principle, electronic integration of peak areas is easily obtained with greater accuracy and precision than by other methods. A complete qualitative and quantitative chromatogram and percentage composition is presented during one run and all component peaks within the 10^{-11} to 10^{-7} A range can be recognized at a glance.

Results and Discussion

Routinely a 1 μ l sample of each gasoline was analyzed by program 2 using the digital log electrometer. Little or no difficulty was experienced in distinguishing between brands and grades of gasolines. Figures 9 and 10 are representations of two separate Shell regular

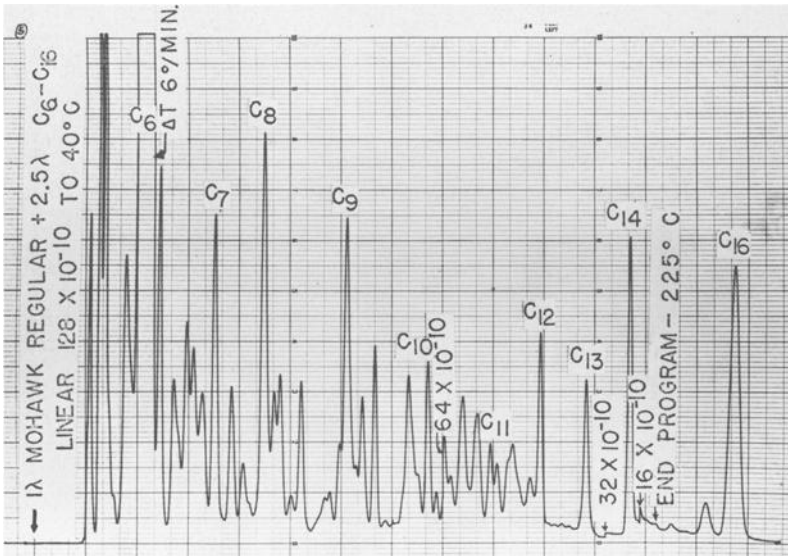


FIG. 5—Linear electrometer presentation of an injection of a mixture of Mohawk regular gasoline and C₆ to C₁₆ hydrocarbons.

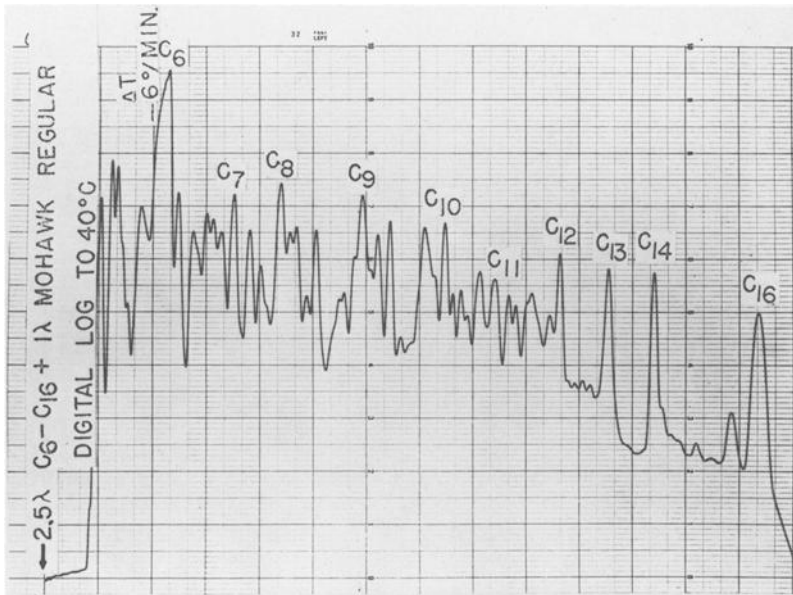


FIG. 6—Digital log electrometer presentation of Fig. 5.

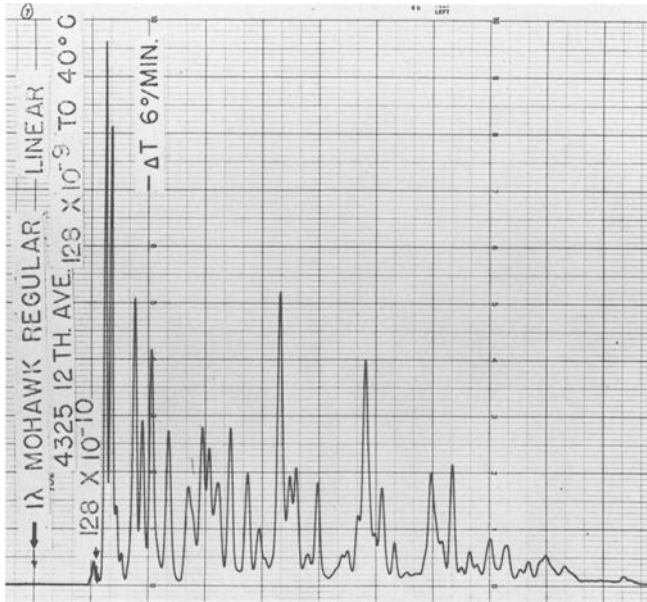


FIG. 7—Linear electrometer presentation of an injection of a mixture of Mohawk regular gasoline without hydrocarbons.

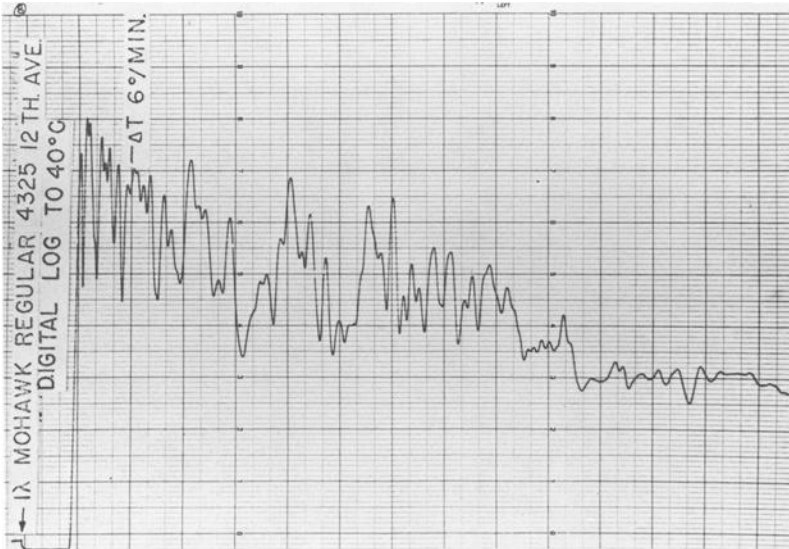


FIG. 8—Digital log electrometer presentation of Fig. 7.

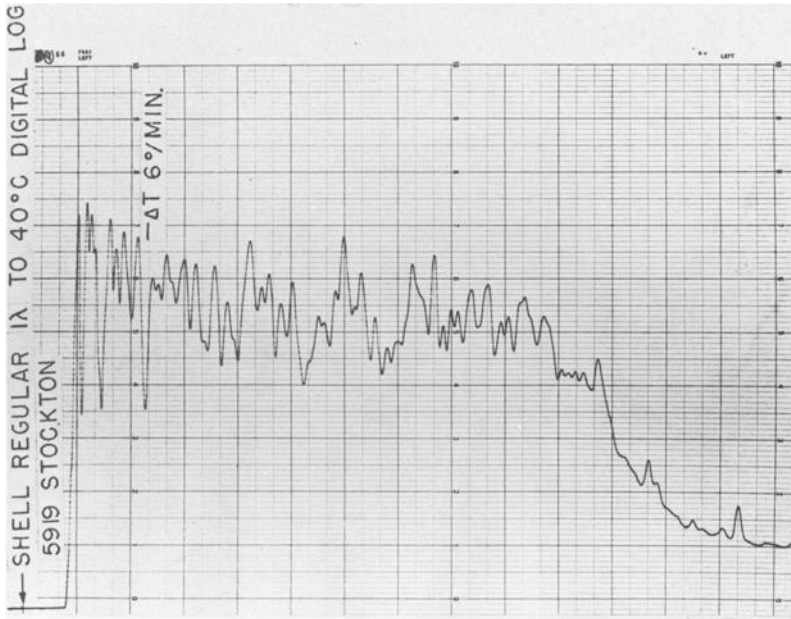


FIG. 9—An injection of Shell regular gasoline from one gas station bulk tank.

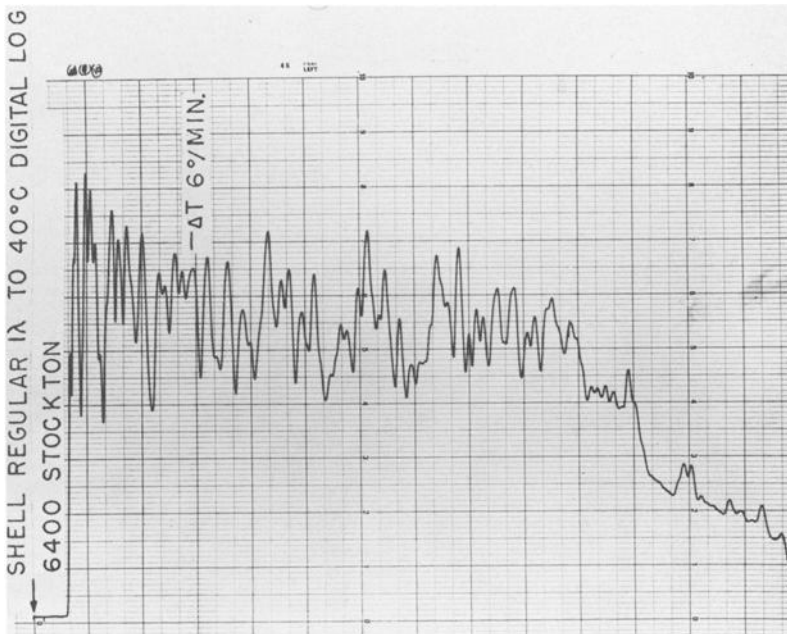


FIG. 10—An injection of Shell regular gasoline from a different gas station bulk tank.

gasoline samples taken from two stations about six blocks apart. It is not known whether the two stations received their fuel deliveries on the same day and from the same bulk truck. The charts suggest identification of the stations is possible, but a sufficient number of samples have not been analyzed to confirm this. Some off-brand gasoline samples gave results similar to the Shell samples, which suggests that they received their supply from the same refinery on the same bulk delivery truck.

Accelerants recovered by steam distillation from burned materials were also identified [5]. Figure 11 illustrates the recovery of 4½ ml of gasoline by steam distillation from 5 ml of Mohawk regular gasoline which had been added directly to water in the still. No appreciable loss of the low boiling fraction was noted. Figure 12 illustrates the results of an analysis of the 0.3 ml of distillate recovered from evaporation, under a hood for 1 h, of 5 ml of Mohawk regular gasoline that had been absorbed by a block of wood. When compared to Fig. 8, it can be seen that the low boilers are lost, as would be expected; however, sample recovered is readily identified as gasoline. Figure 13 illustrates the results of recovering 0.3 cm³ of distillate by steam distillation from a block of wood which absorbed 5 cm³ of Mohawk regular gasoline and burned for 2 min. The results are similar to those in Fig. 12. Program 2 was used during the analyses shown in Figs. 11 through 13.

Other types of hydrocarbons were also analyzed. Examination of the charts showed that the background, which is ignored in the linear electrometer in favor of peaks, was helpful in identifying the type of accelerant.

Several gasoline samples were analyzed by using the capillary column [20–23] and program 3. Figure 14 illustrates the results of one such analysis of a sample of the Mohawk gasoline used in previous analyses. One hundred and forty-two peaks were recorded by the capillary column, as compared to 57 peaks recorded by the 3 percent SE 30 column. However, the analysis time was more than doubled, namely, 102 min was required for elution from the capillary column as compared to 45 min for the 3 percent SE 30 column.

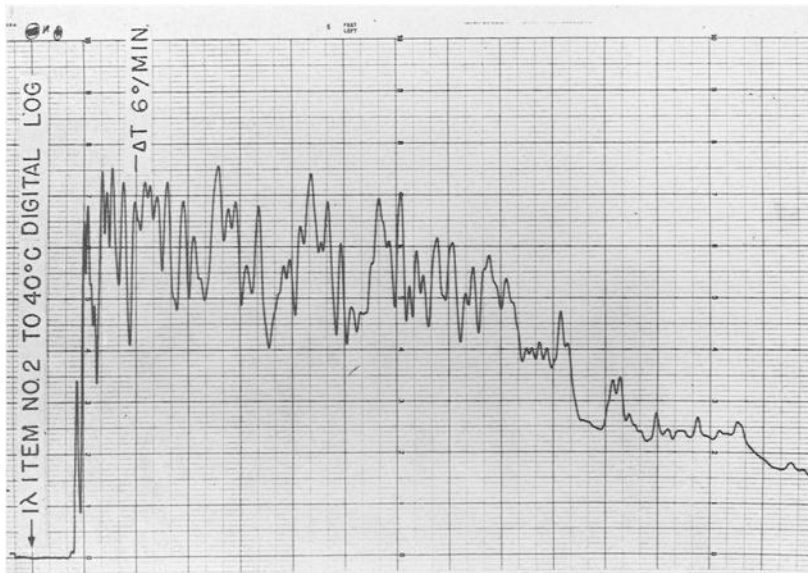


FIG. 11—An injection of a gasoline recovered by steam distillation.

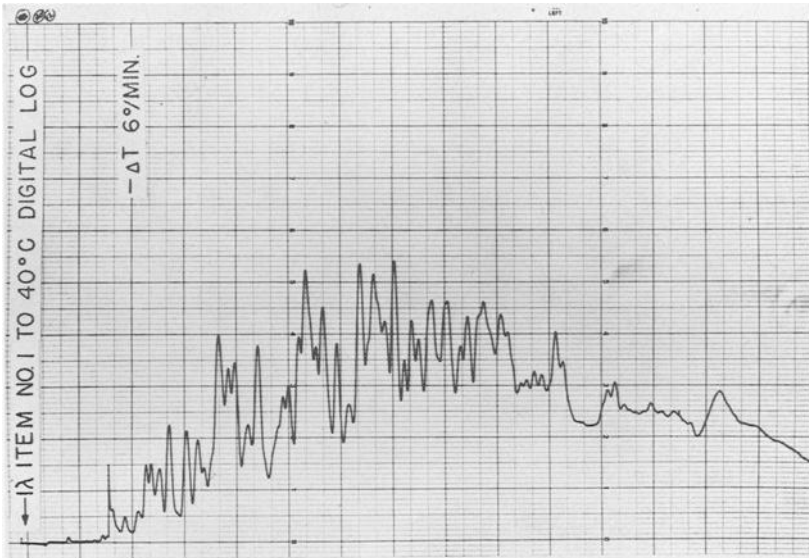


FIG. 12—An injection of a gasoline distillate recovered from wood after allowing it to evaporate for 1 h.

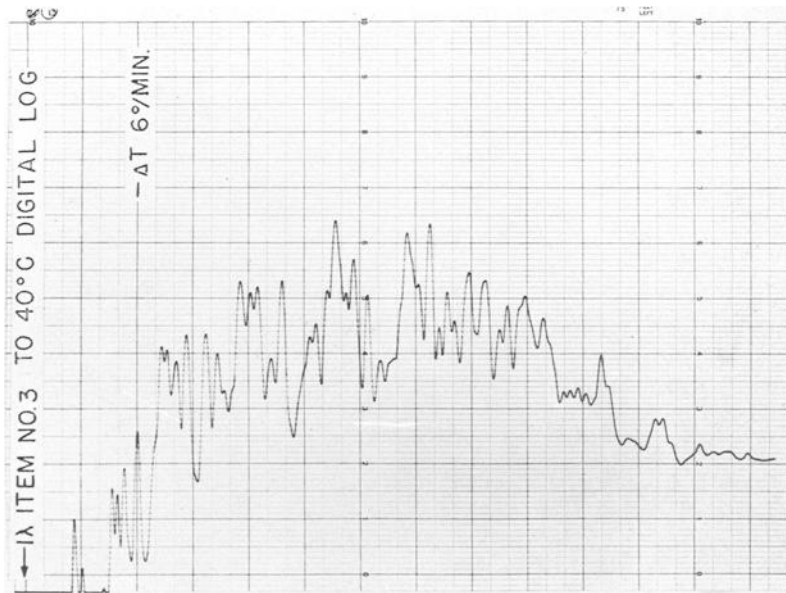


FIG. 13—An injection of a gasoline distillate recovered from wood after burning for 2 min.

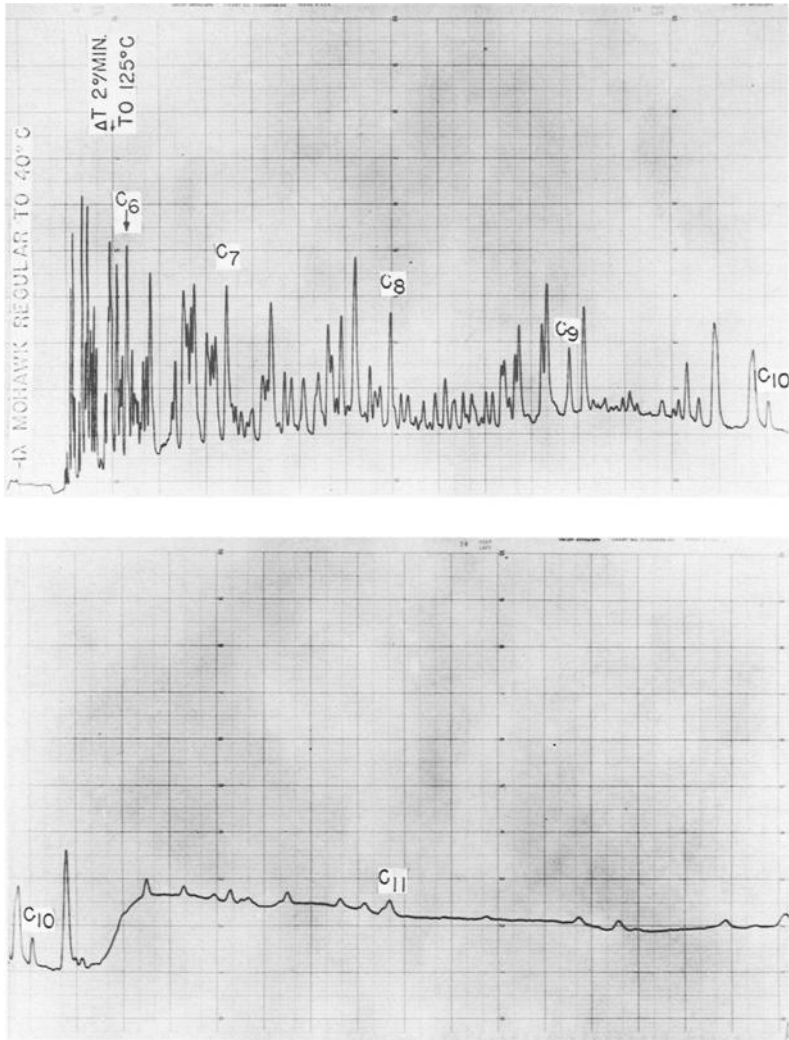


FIG. 14—An injection of Mohawk regular gasoline employing a capillary column.

Thus, employing the digital log electrometer with capillary columns, cryogenic temperature programming, a printout integrator with log display [24–26], and computer data analysis and retrieval considerably improves identification. Furthermore, the wide variance in signal intensities presented by samples analyzed by the technique offer advantages over the linear electrometer in pyrolysis gas chromatographic analyses.

Summary

The digital log electrometer presents a chromatographic pattern which provides a better means for identifying and distinguishing hydrocarbons commonly encountered as accelerants in arson. Only part of its potential has been revealed thus far using conventional columns.

Whereas transients generated by a range change in a linear electrometer may destroy valuable data, logarithmic type electronics can cover four decades of signals without a range change and provide a continuous line graph showing all of the component peaks resolved by the column. Preliminary studies using a capillary column have also been made which indicate that higher resolution is better exhibited by use of logarithmic electronics.

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