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SOME APPLICATIONS OF GAS CHROMATOGRAPHY TO FORENSIC CHEMISTRY*

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Forensic chemistry may be defined as the application of scientific chemical techniques to problems involving legal action with the purpose of aiding the administration of justice. In a crime laboratory, this is accomplished through the assessment of physical evidence which may be plainly visible, but usually is detectable only through the application of very sensitive chemical or physical techniques. Gas chromatography, now one of the most important analytical tools, has excellent capabilities for separating individuals from complex mixtures as well as the preparation of pure compounds for subsequent identification.

EQUIPMENT

Five types of columns are now utilized in gas chromatography, depending upon the nature of the sample to be examined. These are (1) the Craig polyester type, (2) Apiezon M, (3) a polyglycol of 20,000 average molecular weight, (4) silica gel and (5) a silicone rubber column. The ester column (table I) has been used primarily for fatty methyl esters. This is a five foot column operated at 185°C. The Apiezon column is used with flammable materials. It is four feet long and is operated from 90° to 215°C, depending on the volatility of the material to be separated. Alcohols normally are separated on the six and one-half foot polyglycol column at 85°C. The six-inch silica gel column is used for gases at room temperature. Drugs are separated on the 5 foot silicone rubber column at 215°C. Either hydrogen or helium flowing at 100 ml/minute serves as the carrier gas. The detector was in this instance Gow-Mac thermal conductivity type Model TE II, and the recorder a Leeds and Northrup one second one millivolt Speedomax G.

DISCUSSION AND RESULTS

In order to obtain positive identification of a compound or mixture, attention must be given to both major and minor peaks. To accomplish this, the gas chromatographic instrument must couple

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TABLE I

CHROMATOGRAPHIC CONDITIONS

Column Packing	Craig Polyester	Apiezon M	Glycol	Silica Gel	Silicone Rubber
Column Temp. (°C)	185	90–215	85	25	200–250
Column Length (feet)	5	4	6½	6	5
Preheater Temp. (°C)	250	250	150	—	275
Carrier Gas	Hydrogen or Helium				
Carrier Flow Rate	100 cc/minute				
Detector	Gow-Mac Thermal Conductivity Model TE-11				
Recorder	Leeds and Northrup Speedomax G 1 Sec. 1 MV.				

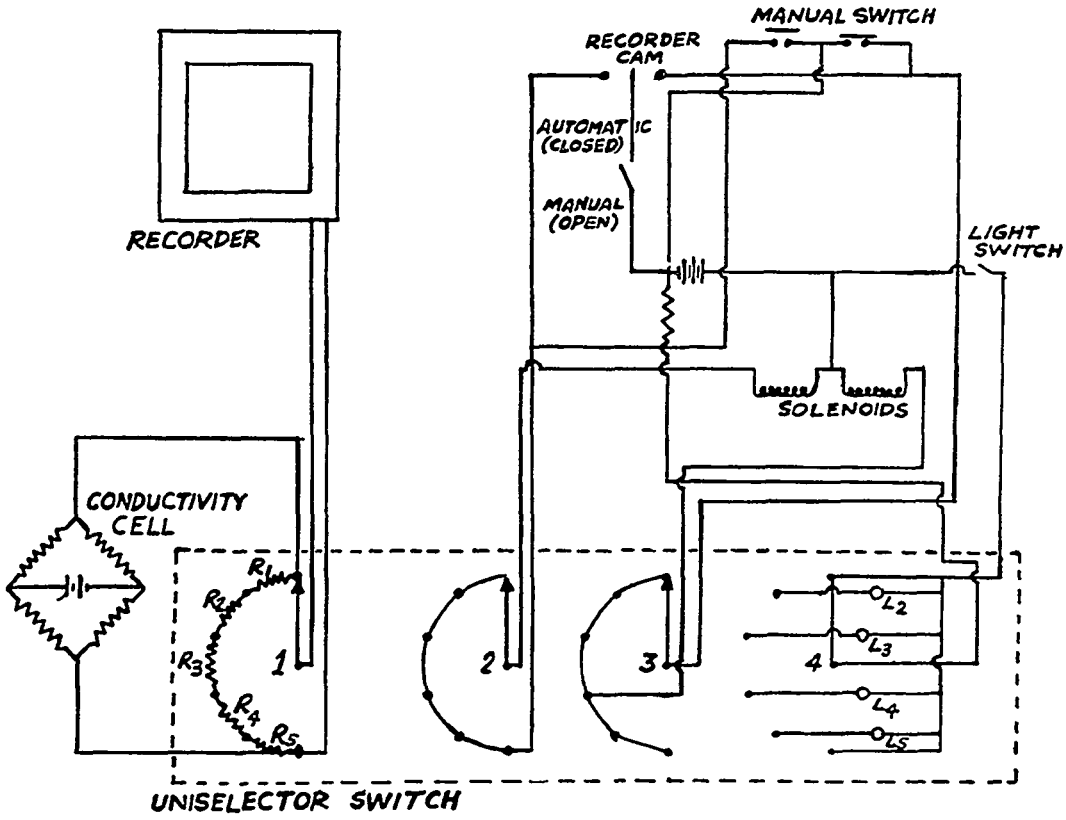

Figure 1
Attenuator Diagram

sensitivity with attenuation such that all peaks, whether major or minor, are shown in proper relation on the same chart. For this purpose a decimal attenuator has been constructed, the details of which are shown in figure 1. The heart of the attenuator is the four-gang Uniselector switch manufactured by the General Electric Co. of England. A similar type of switch is now available from radio supply houses—gang one of the switch contains precision resistors numbered R_1 through R_5. The values of these determine the signal suppression at any corresponding contact and in this case are multiples of 10 of each other, thereby causing attenuation to follow a decimal pattern. The sum of values of all of the resistors should equal the input impedance of the recorder used. Gang two controls the clockwise rotation of the switch arms which results in lesser amounts of attenuation. The most clockwise position ot this gang is not wired in order to prevent the switch from moving below zero attenuation and losing its signal.

Gang three controls up-scale movement, and here the most counterclockwise contact is not wired to prevent the switch from losing the signal on its high end. The contacts of gang four are wired to corresponding dial lights. These show which range or scale is functioning. The base scale, with zero attenuation, is not wired through an indicator light in order to save battery current, since most of the time the instrument operates on base range. The actual changing of ranges is accomplished by means of two solenoids in the switch; one to shift downward and the other to shift upward. These can be actuated by fiber cams on the slide-wire shaft of the recorder, or, they may be operated by means of manual switches. The signal from the attenuator is recorded by the Speedomax G recorder with the signal to the attenuator being furnished by a Gow-Mac thermal conductivity cell.

Typical Problems

Alcohol. The criminologist must characterize the chromatograms of the lower alcohols over wide concentration ranges. These extend from the 50

percent liquor samples to 0.1 percent in blood samples. In the liquor sample, automatic attenuation is especially useful since here the minor peaks can establish the brand as well as the type of beverage. The minor peaks are fermentation products other than ethanol, such as acetone, acetaldehyde, ethyl acetate, methanol, propanols, butanols, and higher alcohols.

Alcohol in blood is a completely different problem from alcohol in the bottle. In blood, ethanol is the only peak to be determined, and since the expected concentration runs from 0.1 to 0.2 percent, high sensitivity must be achieved. If the blood sample is first extracted with acetone, blood solids coagulate and need not be filtered from the solution prior to injection into the chromatograph. Acetone does not interfere with the alcohol determination.

Ethanol is not the only alcohol of importance to the criminologist. Methanol also is encountered. This lightest of alcohols may be determined under the same conditions as have been set forth for ethanol and higher alcohols.

Drugs. The problems met in the analysis of drugs are many and varied. Some of the most frequent are:

a. Analysis of mixtures for one or more components.
b. Chemical identification of individual substances.
c. Identification of small quantities.

Gas chromatography has what it takes to aid the forensic chemist in all of these problems. It has the ability to separate complex mixtures, and with special techniques pure samples may be collected for positive identification. Incidentally, positive identity cannot be based on retention time alone. In order to chemically identify a substance, it must be isolated in pure form and compared with known compounds using standard physical and chemical techniques.

Parker and Kirk[1] separated and identified some 23 barbiturates, and each produced its own single peak. These eluted compounds may be collected by dissolving in a suitable solvent and reserving for positive chemical identification. This is accomplished employing a technique developed by Walsh and Merritt.[2] A color spot test is employed with the eluted sample at the time of collection. Spot test reagents for the various drugs are extremely sensitive, with identification limits ranging from one to 0.001 ug.[3] The quantity of sample dissolved from the eluted peaks may be increased if necessary by repeated injection and collection. Barbital was separated from thiopental on a five foot aluminum column using silicon rubber on firebrick. The sample was collected by bubbling through a test tube containing acetone and glass beads. The dissolved eluted sample was concentrated by evaporation on a steam bath and recrystallized. Evaporation should be carried out in a glass well, or, from a high boiling solvent to obtain well-formed crystals. At least 0.01 micrograms of sample must be collected for recrystallization. The recrystalized sample is examined with a polarizing microscope equipped with a Kofler Hot Stage. The following properties have been observed on this collected sample and are shown in table II. With these chemical, physical, and optical properties we have fingerprinted this eluted peak and identified it positively as that of barbital.

TABLE II

PROPERTIES OF ELUTED SAMPLE

Collected Sample	Barbital
a. Soluble in acetone	a. Soluble in acetone
b. Birefringent	b. Birefringent
c. Sublimes	c. Sublimes
d. Melting point 188°C	d. 188°C
e. Polymorphic	e. Polymorphic
f. Eutectic melting point (Salophen) 163°C	f. Eutectic melting point[5] (Salophen) 163°C

Gases. The gases most commonly encountered by the forensic chemist are carbon monoxide, carbon dioxide, light hydrocarbons, cyclopropane, and ether. Carbon monoxide and carbon dioxide are usually absorbed by blood from an environment of partial combustion. Light hydrocarbons, though much less soluble in blood are more toxic than carbon monoxide. Cyclopropane and ether are common anesthesia and can be obtained in many clinics and hospitals. All of these gases are best detected at room temperature; the hydrocarbon types on the Apiezon column and the other gases on either molecular sieve or silica gel. Water and blood solids are irreversibly absorbed on the silica gel and molecular sieve columns thereby making necessary frequent replacement of the column

[1] PARKER, K. D., KIRK, P. L., ANALYTICAL CHEMISTRY *33*, 1378 (1961).

[2] WALSH, T., MERRITT, C., ANALYTICAL CHEMISTRY *32*, 1378 (1960).

[3] STEWART, C. P., STOLMAN, A., TOXICOLOGY Vol. II, p. 242. Academic Press, New York, 1960.

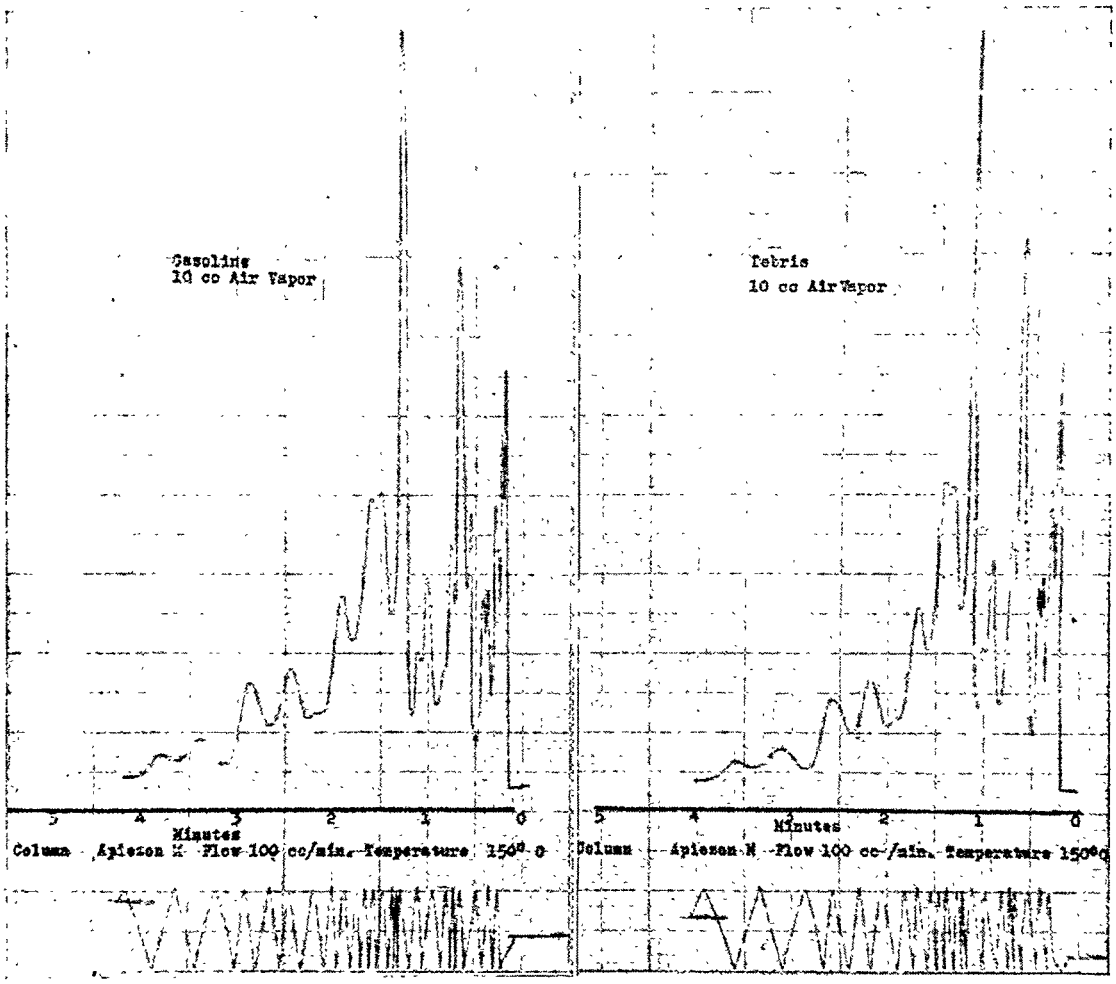

Figure 2

packing material. Water may be removed from samples injected into the Apiezon column using a precolumn either with calcium carbide or calcium hydride. If such a precolumn is utilized it must be heated at least to 100°C, to prevent absorption of part of the hydrocarbon sample.

Flammables. Flammables are the number one tool of the arsonist. Fortunately, evidence of their use is not completely destroyed even for flammable material of high vapor pressure, or when the environment has been elevated at temperature for several hours. Types of materials to be expected include gasoline, paint thinner, charcoal lighter, turpentine, paint remover, fuel oil, kerosine, and the like. None of these materials are single compounds but definite mixtures, and for this reason identification may be established by preparing a chromatogram which covers not only the major ingredients, but also the minor ones including impurities. Here an automatic attenuator may be of tremendous service. Comparing entire patterns rather than single peaks eliminates much uncertainty. The pattern shown in figure 2 was obtained from rags found at the scene of a fire after the fire had been extinguished. The rags were water saturated, burned, and loaded with debris from the building. Only the odor of burned building was evident to the nose. The rags were placed in a can, and 10 ml. of vapor were withdrawn slowly by means of a six-inch needle inserted into the rag bulk. This vapor sample was then injected onto the Apiezon column operating at 180°C. A similar chromatogram was prepared employing a vapor sample drawn from a container of gasoline. The position and relative size of all the peaks in both chromatograms indicate that the samples used

TABLE III

FATTY ACID DISTRIBUTION OF SOME TYPICAL FATS

	Lauric	Myristic	Myristoleic	Palmitic	Palmitoleic	Stearic Oleic	Linoleic Linolenic
Pork.....	0.4	0.9	0.1	31.0	0.1	66.9	0.5
Beef.....	0.3	3.0	0.2	29.0	1.4	65.8	0.3
Lamb....	0.9	1.9	0.2	25.0	1.3	70.7	0
Veal.....	2.4	4.2	0.3	30.1	1.1	61.0	0
Horse....	2.1	0.9	0	30.3	0.3	66.0	0.4
B48.....	0.9	1.5	0.8	19.6	7.3	58.1	15.5
W55.....	0.7	1.3	1.1	16.1	11.4	50.2	19.0
B32.....	1.6	1.3	1.0	16.3	9.6	51.2	19.0

were similar. A current file of chromatograms of flammable materials can indicate to the investigator the type of material used, possible sources of the material, and, in certain cases, the age of the material.

Fats. Table III shows the fatty acid distribution of a few typical fat samples. The top five are from animals; the lower three are human: a 48-year old Negro, a 55-year old White, and a 32-year old Negro.

The samples were prepared for chromatography by saponifying with alcoholic KOH and refluxing for a few minutes on a steam bath with a solution of boron trifluoride in methanol according to the method of Metcalfe.[4] The fatty methyl esters so prepared then were chromatographed at 185°C, on the Craig polyester column. From the fatty acid distribution, it is apparent that human fat contains more unsaturation than animal fat. This can be observed in the myristoleic, palmitoleic, and linoleic fractions. Also, human fat contains only about one-half as much palmitic acid as does animal fat.

Sufficient evidence is not currently available to establish definitely the relationship between different samples of human fat; however, as humans age, it would appear that the lauric acid content of their fat decreases. It would appear too that whites have more unsaturation in their fat than Negroes.

The future of gas chromatography in forensic chemistry projects further than can be visualized at the present time. In addition to the applications mentioned in this paper, such materials as perfumes, coatings, plastics, oils, solvents, and poisons readily lend themselves to chromatographic analyses.

[4] METCALFE, L. D., SCHMITZ, A. A., ANALYTICAL CHEMISTRY *33*, 363 (1961).