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PRESENT STATUS OF GAS LIQUID CHROMATOGRAPHY IN THE CRIMINALISTICS LABORATORY

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From time to time, a new technique which is developed for other purposes assumes unique significance for the investigative laboratory. In recent years there have been a number of such developments, but of all of them, gas liquid chromatography (GLC) has provided the most immediately useful and broad applications. It is the purpose of this article to outline them and to provide some guidelines to their application to a variety of types of evidence.

Not only does the method originated by James and Martin (11) have value with materials commonly recognized as gases and vapors, but to a large variety of materials that are solid at ordinary temperatures and with high melting points. Thus, it was shown by Drs. VandenHeuvel, Sweeley, and Horning (30) that certain high boiling and non-polar tube fillings, especially SE-30, would serve to separate mixtures of steroids, and this work was extended to alkaloids in a paper by Lloyd *et al.* (19). Later applications of this material to the separation of a wide variety of drugs and synthetics have been successful. Aside from the highly polymerized materials which decompose at considerably lower temperatures than those necessary to volatilize them, it now appears that most organic compounds are susceptible to separation and isolation by some variation of GLC conditions. Even the polymers may be studied through pyrolysis and direct GLC separations of the products, which allows excellent identification, and even quantitation (3, 28, 29).

THE NEEDS OF THE CRIMINALISTICS LABORATORY

An investigative laboratory has somewhat different needs than most other laboratories.

Identification of pure mixtures and materials and determination of source are both important goals, although GLC has greater application to the former. Quantitative analysis is generally of secondary importance, except in a few instances, such as blood alcohol determinations. Identification of a pure compound by a single GLC run is no more reliable than by paper chromatography, melting point, or other characteristic physical constant, since only a retention time is measured. A combination of runs can yield significantly more information, as parameters related to boiling point, functional groups and internal bonding structure can be elicited with the proper combination of columns. The situation is quite different with pyrolysis, and identification within specific groups can be quite reliable. If the original substance is a complex mixture, it is possible to make an identification from a gas chromatographic separation of the components, followed by an analysis of one or more collected components by other means, as infrared or mass spectrometry. Versatile as the GLC methods are now known to be, it is certain that developments of the future will outweigh those of the past, and that no criminalistics laboratory can long afford to forego the utilization of these methods.

GENERAL CONSIDERATIONS OF GLC

Detailed treatment of the theory and basic considerations of GLC is available elsewhere (15, 17, 18) and will not be duplicated here. Fundamentally, the principle is not different from that of any other form of chromatography, except that the mobile phase is a gas (carrier gas), and the emergent fractions are detected by completely

different means than with other forms of chromatographic separation, since each fraction is a gas or vapor. The detection process tends to be less specific in GLC than in paper chromatography, but will generally respond to a wider variety of materials, thereby giving a more universal application with a single detection procedure.

All instruments contain a few simple components, often with quite elaborate accessory electronic amplifying and recording equipment. The simple components are as follows:

1. A source of carrier gas, such as helium, hydrogen, nitrogen, argon, or steam, delivered under closely controlled pressure and generally in a pure form;

2. A sample chamber into which a gaseous, liquid, or solid sample may be introduced at a selected temperature;

3. A column in which separation occurs, consisting of a tube of metal, glass, or other less common material, and containing a relatively inert granular solid support carrying on its surface a very thin layer of relatively non-volatile liquid (or the tubing wall is coated with a thin layer in a capillary column), and operated at a controlled temperature;

4. A detector which will give some sort of response to changes of composition of the carrier gas; and

5. A recorder or indicating instrument generally along with its electrometer amplifier, the function of which is to convert the signal from the detector into some indication useful to the operator, such as a line graph.

The necessary accessory equipment consists of the various temperature controls, meters for measuring the gas flow, and the circuitry associated with the detector and the recorder. Additional accessories that are optional include temperature programmers which allow predetermined alterations of temperature, collecting accessories to collect the separated fractions as they emerge, pyrolysis units to decompose organic materials prior to chromatographing the products, and a variety of instruments designed to provide additional identification of individual fractions. The latter may utilize mass spectrometry, infrared absorption, or other physical or chemical properties. Such special instruments are not commonly employed except for very special types of research investigations.

With all of the possible variations in equipment and choice of analytical conditions, it is important to keep in mind the limited needs of the criminalistics laboratory, as compared with those of certain specialized research laboratories. It is also important to realize that the various components and conditions are not totally independent of each other, and the choice of a detector, for example, may limit the type of carrier gas, the character of the sample, and other details of the operation. The choice of a stationary liquid phase in the column will determine not only the types of material that can be separated, but the upper temperature limit of operation, and this, in turn is related to the volatility characteristic of the sample. Thus, the choice of the analytical system and its operating parameters is a single problem with various inter-related parts. Without detailing all of these, the following considerations will include suitable arrangements for various applications.

The Detector. A constant stream of carrier gas will flow through the detector, interrupted at intervals by admixture of other gases or vapors. The detector will be required to sense this alteration of composition and to be responsive to extremely minute differences. The latter requirement is necessary if the optimal separations are desired, because the separation becomes more efficient as the sample size is decreased and where trace components are to be detected. Thus, every increase in sensitivity of a detecting system makes possible an increase in the number of types of samples that can be chromatographed. This fact has sometimes been minimized by operators who have no deficiency of sample, and see no reason for proceeding to the smallest possible samples.

There are many types of detectors that will sense differences in composition. They are not equal in sensitivity, and they tend to respond differently to different types of gases and vapors. Of these various detectors, it seems that only three have a practical place in the criminalistics laboratory at this time—the catharometer, the hydrogen flame ionization detector, and the electron capture detector. The catharometer, which utilizes the property of thermal conductivity, has been the most widely used. The most common type of catharometer is that utilizing a heated wire over which the carrier gas passes. With a constant flow of the carrier gas, a constant transfer of heat away from the wire is maintained. When the composition of the carrier gas alters, its thermal conductivity

and specific heat will alter depending upon the contaminating substance, and more or less heat will be conducted away from the wire. This alters the electrical resistance of the wire, and the resultant change in the heating voltage across the wire is detected or measured in a Wheatstone bridge arrangement.

The effect of the carrier gas on the operation and sensitivity of the catharometer is somewhat complex. A major factor is the thermal conductivity of the carrier gas—the higher the thermal conductivity the greater the sensitivity as a rule. Helium, hydrogen, and nitrogen are popular carrier gases; helium is probably the best choice for general application with the catharometer, as it gives the best compromise for a number of factors.

The main advantages of the catharometer detector are the wide range of substances to which it will respond and its non-destructive detection of the fractions, thus allowing collection and further analysis. Its main disadvantage is its relative insensitivity compared to other types. A secondary disadvantage at times, especially in the criminalistics laboratory, is its sensitivity to water. If a laboratory is to be restricted to a single detector, the catharometer is not the one of choice for general utility.

The hydrogen flame detector is probably the most generally useful of the mentioned three for use in the crime laboratory. The carrier gas, which is usually nitrogen, is passed directly from the column through a small hydrogen flame. When combustible vapors are carried through the flame with the carrier gas, they are burned with the resultant production of ions. The exact mechanism of the formation of the ions is not completely understood at this time. Two electrodes with an applied potential are positioned so that the production of these ions increases the conductivity of the space between them, thus allowing a small increase in the current. This increase is detected and amplified with the electrometer associated with the detector and then generally recorded with a differential recorder. The detector is continually swept clean by a rapid flow of air through it, which also supplies the oxygen for combustion. If pure oxygen is used for this purpose instead of air, a significant increase in sensitivity can be realized, which carries along with it an undesired increase in the background noise.

The main advantage of the hydrogen flame detector is its great sensitivity for those substances

to which it will respond. Its negligible response to water is also an advantage at times, such as when it is desired to detect alcohol in blood without a preliminary treatment to remove the water. Its relative insensitivity to several other substances is, for the most part, of little or no practical importance to the criminalist. A possible disadvantage of its destructive detection is neutralized by the availability of splitters which will route part of the effluent stream away from the detector for collection.

In a laboratory doing toxicological work involving pesticide analysis, the electron capture detector would be a desirable addition. In this device, a stream of nitrogen (or other) carrier gas is bombarded by beta rays from a tritium (radioactive hydrogen) source which ionizes the nitrogen molecules through loss of electrons. A sufficiently low potential is applied to two electrodes to just collect the ions and electrons to produce a "standing current." When certain types of molecules are mixed with the nitrogen, they will attract (capture) the electrons and thus become negative ions. These negative ions then recombine with the positive ions at a far greater rate than do the electrons, thus reducing the number of ions available to carry the current. This causes a reduction in the current flow, which is measured by the auxiliary equipment.

There is a very considerable selectivity of response by the electron capture detector, and, for many substances to which it does respond, its sensitivity is extreme, e.g., in the picogram range. Such is the case for halogenated compounds, and thus the usefulness of this detector in pesticide analysis. This high sensitivity and selectivity is an advantage for specialized work, but puts the detector at a disadvantage as a single detector for general work. It can be used in conjunction with one of the other detectors to provide additional parameters for interpreting results.

Another detector that has been used for a considerable amount of work, but which does not offer any additional advantages over those mentioned is the argon detector. This was one of the earliest ionization detectors that found widespread use, and is characterized by the instrument produced by *PYE*. In this type of detector, ionization is produced in the gas stream by beta rays produced by a variety of radioactive sources, such as Sr^{90} . The ions are collected on highly charged electrodes. Argon, which is generally used as the

carrier gas, may be excited to a metastable state, which does not add to the conductivity of the cell, but which has a sufficiently high energy to ionize most other molecules. When coming in contact with other molecules, the excited argon molecules will ionize them, thus increasing the conductivity of the gas in the cell. The detector contains some 10 millicuries of radioactive material, which constitutes a potential hazard, and few manufacturers produce instruments built around this variety of detector. Also, certain contaminations in the argon stream, such as water, will significantly decrease the sensitivity of the detector. Aside from these disadvantages, the principle is a very favorable one, and the sensitivity under favorable conditions can theoretically be somewhat higher than the flame ionization detector, although this is rarely realized in practice.

Choice of Instruments. Inasmuch as all instruments may be equipped with a variety of column types, and these may be charged with any desired filling, the major point in the choice of an instrument is the type of detector, with several other considerations also being of importance. One very important aspect to consider is the convenience of changing columns. The fittings should be easily reached, and there should be enough room to manipulate a wrench for tightening or removing the nuts. Also, if a flame ionization unit is considered, the flame detector should be easily removable for cleaning. This is a necessary chore to perform somewhat frequently for a busy instrument, for the detector can become quite noisy after a while if this maintenance is neglected. Another point to consider is the upper temperature limit of the instrument. While lower temperatures are adequate for volatiles, temperatures up to 400° C are needed for versatility. Although such high temperatures are seldom used for the actual separations, it may be needed for column conditioning and other important functions. At this time, there are a wide variety of excellent instruments available from several manufacturers, and it is useless to base a choice on any other criteria than instrument type, price, available servicing, and factors as those mentioned above. There are, however, two possible philosophies to follow, and it is important to consider them.

In one, manufacturers have striven to produce an all purpose instrument with multiple columns, a choice of detectors, and accessibility of numerous supplementary items, all in one instrument. In the

other, the instrument is kept as simple as possible with single column fittings and one detector. The difference in price of the classes of instrument is very considerable, but often, two complete instruments of different type cost little more than a single more complex instrument, and, in some instances, even less. Insofar as the crime laboratory is concerned, the difference is important. If never more than one person will be doing gas chromatographic work at one time, the combined instrument offers obvious advantages. If two or more persons may be doing it, or if the variety of work calls for several column fillings, it is very often advisable to utilize two or more of the less expensive simple instruments, so that more than one person may work at one time, and a variety of column packings and detectors may still be quickly available. There is often a significant saving of cost under these circumstances.

At the time of writing, a simple instrument utilizing either a hydrogen flame or TC detector can be purchased for around \$1,000. A recorder will run around \$600. Other necessary equipment may run from \$100 to \$500, depending upon the needs of the laboratory. Thus the total initial cost is likely to be in the neighborhood of \$2,000. Periodic costs will be incurred for carrier gas, columns, and column packing materials for a do-it-yourself laboratory. The more complex instruments and accessories will run in the neighborhood of \$3,000 to \$5,000 and up.

The most practical recorder has been found to be one with a full scale response of 1-mV, or one with a variable scale setting which includes a 0- to 1-mV range. This will give a steady baseline with a well maintained instrument, and the electrometer output can always be attenuated if less sensitivity is desired. The addition of a *disc* integrator may be desired for determining the areas under the peaks in quantitative work. A digital integrator would seem to be the most desirable method of integration, but the cost of these is somewhat prohibitive at this time for the general criminalistics laboratory.

The requirements for flow regulators for the carrier gas depend to a large extent upon the type of detector used. For maximum versatility, a regulator that will be adequate for a thermal conductivity detector should be obtained even though a flame ionization detector is the sole one used at the time. The regulator should have a pressure reducing system followed by a good needle valve.

If a flame ionization detector is used, a source of hydrogen must be available. Hydrogen can be obtained in gas cylinders, in which case an additional flow regulator will be required. For reasons of safety, the cylinders may have to be kept outside of certain buildings, and the hydrogen brought into the laboratory through flow lines. To avoid the hazards of hydrogen cylinders, a hydrogen generator may be obtained. This produces hydrogen by means of electrolysis of water, and the hydrogen is never under any more pressure than required to push it through the detector at a given flow rate. These generators are still somewhat expensive, however, and have not been in use for a sufficient time to determine if the advantages and longevity of operation justify the additional cost.

Columns. Columns can be divided into preparative and analytical categories, and the latter can be further divided into packed and capillary (Golay) columns. Preparative columns are useful when quantities of material separated by the gas chromatograph are to be collected for further analysis or other purposes. They are usually of a larger diameter and have a higher percentage of stationary phase than the analytical counterparts. The use of preparative columns in the general criminalistics laboratory is relatively limited, although instances can occur when they will be very helpful. The detector of choice for preparative work is the catharometer.

The packed analytical columns, which are generally $\frac{1}{8}$ or $\frac{1}{4}$ inch in diameter, can handle a wider range of concentrations of the injected material than the capillary columns, but can rarely be made to have the separating efficiency of the capillary columns (although the same efficiencies are theoretically possible). The capillary columns are considerably more expensive than packed columns, and, being generally made of thin glass tubing, are quite fragile. The packed columns are quite adequate for most work in the criminalistics laboratory.

The column itself may be copper, aluminum, or stainless steel tubing, which can be purchased from a variety of sources. The tubing can be cut to the desired length, filled, and then wound or shaped to fit the instrument right in the laboratory. Or the column may be made out of glass, in which case it will have to be made by someone with the proper equipment and skill. There are some disadvantages with using glass columns if the instrument takes a coiled column. Breakage is

an obvious one, and a considerable amount of attention to the packing process is necessary in order to obtain uniformity of the packing material throughout the column. However, it has been noted with increasing frequency that better results can be obtained in many instances when glass tubing is used rather than metal. It seems that metals have an adverse effect on the properties of the separation process, and may cause excessive tailing of the fractions. There is insufficient evidence to claim that glass columns will give universally better results, but their use is something a laboratory will do well to keep in mind. In some types of work, such as pesticide analysis, the use of glass columns is almost mandatory. Another point to keep in mind, is that other metal areas of the instrument through which the sample passes may have adverse effects. Thus, some sort of glass protection may be desired between the injection area and the column, and from the column to the detector. A simple insert for the injector may suffice, although there are some points about its operation that are not clear yet, such as whether or not some material will flow outside the insert, etc.

The length of the column is another point to consider. A longer column will generally give greater distances between fraction peaks, but also takes longer to complete a particular separation. What is desired is a balance between the time for an analysis and the separation desired. Columns somewhere around five feet in length are commonly used, and seem to be adequate for most general work, although special cases may require shorter or longer columns.

Column Packings. At this time, there is available a bewildering array of column packings, both as regards support material and stationary liquid phase. Fortunately, the interrelation of column packing and detector type is generally of little or no consequence, and almost any type of column packing may be used with any detector provided operating conditions are kept within tolerable limits of control. For instance, the electron capture detector is especially sensitive to thin films of deposited material that may come from column bleeding, and more care is necessary with this detector than with the others. Also, a column can generally be used at higher temperatures with a thermal conductivity detector than with a flame ionization detector because of the sensitivity of the FID to bleeding.

Support materials are generally crushed fire-

brick, Celite (a form of Kieselguhr), glass beads, and Teflon beads. The first two present a larger surface for the liquid phase than the latter two, and are generally more efficient. However, many compounds tend to be adsorbed on active sites in firebrick and Celite (firebrick being far more adsorptive than Celite), and better results may be obtained by using the less efficient supports unless some method of covering the active sites, such as silver coating, is used. The mesh size of the particles is important chiefly in that the resistance of the packing must be kept low enough to allow the gas to flow freely, the column must be packed firmly enough to prevent voids, and it should offer maximum surface for the separation. Probably the best particle size is the 60/80 mesh for columns less than ten feet in length, and a somewhat larger mesh cut for longer columns (24).

The stationary liquid phase is most critical because it is this material that exchanges molecules with the surrounding gas phase. With experience, the chromatographer will choose the phase that produces the best results with his system. However, some degree of standardization should be agreed upon if any large body of related data is to be collected, especially for exploratory and general identification work. Some of the more use-

ful general liquid phases are listed in Table I, along with some of their characteristics and uses.

A guiding principle that may be utilized in choosing a filling is that the retention of any compound is related to its similarity of polarity with the liquid phase. Thus, a non-polar material such as a hydrocarbon will be retained longer by a non-polar phase in which it is more soluble than in a polar phase, and the reverse will be true with a polar phase. In general, very long or very short retention times are not desirable, and the most generally useful phases are those of intermediate polarity.

Conditioning a column material after packing the column is important for best results. Generally, conditioning is done in the gas chromatograph by keeping a slight flow of carrier gas through the column, which is kept near the upper temperature limit for 8 hours to two days. Other variations are noted in the literature for various applications. Proper preparation, packing, and conditioning can make quite a difference in the performance of a column; thus, one should not dismiss a stationary phase material because the column does not function properly at first. Unfortunately, the actual mechanics of getting a column into proper operation are not known exactly, and different persons

TABLE I
SOME LIQUID PHASES AND THEIR CHARACTERISTICS

Liquid Phase	Type	Temp. Limit*	Solvent	Uses
1. SE-30†	Silicone Non-polar	400°C	Chloroform or toluene	General purpose. Moderate to high temperatures.
2. SE-52†	Silicone Slightly polar	400°C	Chloroform or toluene	General purpose. Moderate to high temperatures.
3. QF-1	Silicone Polar	225°C	Acetone	General purpose. Moderate temperatures.
4. XF-1150	Silicone Polar	300°C	Chloroform or toluene	Polar materials, as amines, steroids, and hydroxy compounds.
5. Carbowax 20M	Polyglycol Hydrogen bonded	225°C	Chloroform or methanol	Oxygenated compounds and nitrogen compounds; water, combustion products; solubility of hydrocarbons is low.
6. Hallcomid M-18	Polar	150°C	Chloroform	Alcohols, nitriles, pyrolysis products.
7. Squalane	Hydrocarbon Non-polar	150°C	Hexane or toluene	Hydrocarbons, ethers, ketones halides.
8. Diisodecyl Phthalate	Diester Moderately polar	150°C	Acetone or chloro- form	General applicability.

* For thermal conductivity detector. Lower at least 50° for a flame ionization detector.

† These liquid phases are probably the most useful for general toxicological screening of non-volatile organics.

may find that different methods work best for them. Often a new column will give poor results until several injections of substances similar to those to be separated have been made. It seems that a column's performance is dependent on its past history of use in addition to the above factors.

Operating Conditions. The column temperature at which a given separation or analysis is run should be adjusted so that the fractions of interest will not emerge too soon or too late. As a general guide, less than 15 to 30 seconds is too soon, and longer than 30 minutes to one hour is too long. The upper temperature limits are set by the liquid phase and the type of detector as well as the desired separations. If the liquid phase is not actually a liquid at the operating temperature, the results with many substances may be somewhat erratic and unpredictable, or the efficiency of the column may be low. This effectively sets lower limits to the use of such liquid phases. The lower limit for a particular phase that is solid at room temperature can be roughly determined by examining a small bit of the phase on a melting point block and noting at what temperature it melts.

The temperature of the injection area should be kept higher than the column temperature if provision is made for this on the instrument. Somewhere around 50° C higher is a reasonable figure. The detector should also be kept at a temperature somewhat above the column, perhaps from 20° to 40° C higher. These precautions will avoid unwanted condensations at awkward moments of the materials to be separated.

For critical work, the gas chromatograph should be kept in an area that is free of drafts and fluctuations of temperature. The combined effect of such changes on the operating temperatures and the electronic equipment can cause trouble. Provision should also be made for a constant voltage supply, especially in a building where other electrical equipment is operating. Mechanical vibration is also to be avoided.

The flow rate for the carrier gas should be determined for the particular conditions by experiment. This can be done by using the following formula:

$$P = \frac{L}{w}$$

where L is the retention time and w is the width of the peak at one-half of its height. To determine the best flow rate, one of the compounds to be separated should be chromatographed at several

different flow rates, such as from five to sixty cc/min. and up in increments of five or ten cc/min. P is determined for each flow rate, and that rate giving the highest value is selected. For best operating conditions this should be tried at various temperatures which allow a reasonable running time.

SPECIFIC USES IN THE CRIMINALISTICS LABORATORY

Blood Alcohol Determinations. There are essentially two problems connected with BA determinations in the criminalistics laboratory: one, determining the presence or absence of ethanol and other materials such as methyl and isopropyl alcohol, acetone, and other volatile materials; and two, measuring the amount of ethanol present, if any. The use of GLC in the criminalistics laboratory so far has been primarily directed toward the first problem. The separating ability of the instrument makes it not only ideal for determining the presence of ethanol, but for discovering any other substances that might inadvertently be influencing the quantitation step. A few laboratories are also using GLC for quantitating the ethanol; others report that they feel the accuracy is not sufficient and they prefer to use other methods for quantitation, using GLC for screening only, which serves to prevent unnecessary quantitative determinations.

It seems that sufficient accuracy (equivalent to any other methods) can be obtained with GLC for the quantitative work, but more information is necessary to define what the critical conditions are before the quantitative application can be generally recommended. Several factors can influence the results and introduce error. The use of a column packing that does not adsorb the ethanol is critical. Adsorptive behavior is unpredictable and can cause serious variations in the quantitation. Lack of standardization of the preparation of the blood prior to analysis can cause error. This is especially critical for vapor injection techniques.

Cadman and Johns (2) report the use of a mixture of di-isodecyl phthalate, Flexol 8N8, and Carbowax 600 (28% by weight) coated on 40/60 firebrick. (This column can be obtained commercially from Beckman Instruments Incorporated, Fullerton, California.) Goldbaum *et al.* (8) use the same type of column, but sample the vapor above the prepared blood sample rather than injecting an aliquot of the sample or an extract into the gas

chromatograph. Parker *et al.* (26) report the use of castor wax (40%) coated on 60/80 Chromosorb W (acid washed). Hessel and Modglin (9) report some modifications of the previous method and use a polyethylene glycol column. Other liquid phases that have been used in some laboratories are Carbowax 600, Carbowax 20M, and Hallcomid. Standards added to the sample for internal calibration on each run that have been used are ethyl acetate, amyl acetate, *n*-propyl acetate, *n*-propyl alcohol, and methyl ethyl ketone. The choice of internal standard will be guided by the column packing used; desirable properties are reproducibility for quantitative work and separation from ethanol and other volatiles that may be encountered. One laboratory runs about 5,000 routine BA's per year, and currently uses a castor wax column with methyl ethyl ketone as the internal standard; the results have been used in court cases about 80 times in three years.

Compared to other methods of blood alcohol analyses, the gas chromatographic method offers a considerable saving of time and a greater assurance that only ethanol is being quantitated. It is likely that it will become a standard procedure in a few years.

Other Volatiles in Blood, Breath, etc. The gas chromatograph is also ideally suited for the detection and determination of volatile substances other than ethanol (26) that may be of interest in the criminalistics laboratory. Goldbaum *et al.* (8) give a general discussion of some aspects of the analysis of volatiles in biological specimens. Kade and Abernethy (13) report two cases of interest, one involving cyclopropane (used as an anesthetic agent) and another involving illuminating gas. Questionnaire returns mention the detection of gasoline vapors from the lungs of victims in flash fires, natural gas in the lungs of chickens involved in a natural gas explosion, and toluene in glue sniffing cases. Also mentioned was the determination of CO₂: O₂: N₂ ratios in drowning and asphyxiation cases. For the determination of the lighter gases, adsorption columns rather than gas-liquid partitioning columns are generally used, which involves the use of packings such as the molecular sieves.

Arson Cases. The gas chromatograph has been used by many laboratories for the detection and determination of fire accelerants. Some discussion of this is presented by Cadman (1). There is also an extensive list of general references at the end of

this paper. Several factors in examining petroleum products are discussed by Lucas (20). The examination of gasolines is discussed by Parker *et al.* (25).

Non-volatile Organics in Toxicological Analyses of Biological Materials. Techniques for identifying non-volatile organic poisons from biological material have been extensively studied during the past few years, but to date no method has been put into routine operation by any crime laboratory that the authors know of. Considerable success with several groups of compounds has been realized, and it should not be very long before routine procedures are being used for these substances. A general screening procedure is examined by Parker *et al.* (27) which included alkaloids, barbiturates, sympathomimetic amines, and tranquilizers. Similar results are reported by Kazyak and Knoblock (14). Fontan *et al.* (7) discusses some results with the antihistamines. A direct extraction procedure from blood for the barbiturates is discussed by Jain *et al.* (10).

The principle liquid phases used for this type of toxicological work are generally SE-30 and Carbowax 20M; due to the high temperatures needed for a general analysis there is actually very little choice in this matter at this time. Some recent results indicate that SE-52, coated on Chromosorb G, may be slightly superior to the above two liquid phases. Problems in the use of the techniques mentioned in the literature probably stem to a large extent from adsorption effects. The use of glass columns rather than metal ones will reduce tailing to a considerable extent. Newer solid supports are being developed which will have fewer adsorption properties, and this should help the situation to some extent. Chromosorb G (Johns-Manville) is one such solid support which is being tested at the time of writing. Temperature programming methods will probably be necessary for a complete screening of all compounds due to the wide range of volatilities.

Pyrolysis-GLC Identification. Pyrolytic identification is another technique that has not found its way into practical use in many crime laboratories. The pyrolytic degradation (thermal decomposition) of complicated molecules into easily chromatographed fragments is one way to get around the problems involved in directly chromatographing the original compounds. If these fragments are characteristic in some way, they would offer a useful method of general identification. Janak (12)

recommended the procedure for a number of organic substances. Detailed studies of the identification of the barbiturates have been made by Nelson and Kirk (21, 22). The identification of the phenothiazines is discussed by Fontan *et al.* (6). Identification of polymers by pyrolysis-GLC has been given considerable attention in the past few years, and its application to a series of plastics is presented by Nelson *et al.* (23). Several instances of the use of the technique in the identification of paints have been reported, and this application is being considered in some detail at the time of writing. The identification of the alkaloids is also possible, and results of this work are being processed. It is possible that the pyrolysis-GLC identification technique will become a standard procedure of more utility than visible or ultraviolet spectrophotometric methods and almost as much utility as infrared spectrophotometry, and will take a permanent place among the lower cost instrumental methods.

Plant Materials—Narcotics and Related Compounds. It will often be of interest to identify the nature or origin of materials such as opium and marijuana. As mentioned previously, Lloyd *et al.* (19) demonstrated the separation of various alkaloids using an SE-30 liquid phase. Kingston and Kirk (16) used the same liquid phase for the separation of the phenolic components of marijuana. The relative peak heights of the various component alkaloids of opium were investigated as a means of determining the origin samples by Eddy *et al.* (4), who feel that the method shows promise. Apparently no direct GLC method for the determination of the origin of marijuana samples has been reported. Farmilo and Davis (5) have studied methods of determining the origin of marijuana, but report that extensive physical and chemical examinations are necessary.

RESULTS OF GAS CHROMATOGRAPH QUESTIONNAIRES

In order to estimate the extent of current usage of the gas chromatograph in criminalistics and related laboratories, a short questionnaire was sent out to several laboratories. The following information is a summary of that contained in the twenty-six questionnaires that were returned.

Twenty of the laboratories had a gas chromatograph, while two others had one available for use in another laboratory. Only four had utilized the results from GC runs in court: two only a few times and the other two about 50 and 80 times.

Thirteen of the laboratories used the gas chromatograph for blood alcohol analyses, six of which used it only for screening purposes, preferring to use other more standard methods for quantitation. Six of the others used GC quantitation only as a check on other methods (as well as screening), while only one apparently used the quantitative results from the GC alone. Eight laboratories did barbiturate analyses, usually in connection with UV analyses as a check. Fifteen used the GC for detection and determination of fire accelerants in arson cases.

Other uses reported were liquor analysis, explosion residues, general volatiles, pesticide analysis, carbon monoxide in tissues, narcotic quantitation, perfume analysis, and pyrolytic identification (in connection with other methods) of paints and plastics.

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