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SUBJECT: A GAS ANALYSIS APPARATUS:

BASED ON GAS CHROMATOGRAPHIC AND CHEMICAL PRINCIPLES.

AFDELING:

DIVISION: CHEMISTRY.

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FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

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A GAS ANALYSIS APPARATUS:
BASED ON GAS CHROMATOGRAPHIC AND CHEMICAL PRINCIPLES.

The control of the operation of many processes depends largely on the control of the composition of gas mixtures either used as starting materials for, or appearing as products of the reaction.

The most universally applied method for these gas analyses is still the chemical volumetric analysis done, mostly in the Orsat type of apparatus.

This apparatus and the techniques involved have been modified from time to time to improve the accuracy, reproducibility or speed of analysis^{1,2,)} and also to extend the range of gases that can be analysed.

Nevertheless, the method is not entirely reliable as shown e.g. by the investigation initiated by the American Society for Testing Materials in which a large number of laboratories participated by analysing mixtures of gases supplied by the Society.

Some of the conclusions drawn by Shepherd³⁾ in his summary of this investigation were:

1. The determination of carbon dioxide by absorption in potassium hydroxide solution consistently yielded results of high accuracy and reproducibility.
2. The determination of small amounts of oxygen by chemical absorption methods is not quite satisfactory.
3. The determination of hydrogen by conventional methods is not satisfactory. Reported values differed by up to 5%.

4. Average results/....2.

4. Average results reported for the carbon monoxide content of mixtures determined by absorption in different reagents are not in agreement.
5. The values reported for nitrogen differ by as much as 4%.
6. The well known limitations of the chemical methods of determining the hydrocarbons were again clearly illustrated in this investigation.

Even under ideal circumstances, the hydrogen, nitrogen and carbon monoxide results may be unreliable as indicated above and the hydrocarbons cannot be determined individually. Olefines and aromatic hydrocarbons are normally determined by absorption as one group and paraffins by combustion as another group. In the latter determination, the volume contraction as well as the carbon dioxide formed during combustion can be determined and thus it is possible to express the result in terms of two components e.g. "per cent methane" and "per cent ethane". Such a degree of differentiation is inadequate in many cases. Nitrogen is determined by difference or as the residual volume of gas and is therefore also subject to error.

Although the method is relatively simple, considerable experience is needed to produce reasonably satisfactory results and the analysis of a gas mixture containing all the constituents, from carbon dioxide to hydrocarbons, usually analysed by this method takes about two hours.

In the course of time, methods based on differences in one or another physical characteristic of the relevant gases have been developed. While some of these yield excellent

results/.....3.

results the apparatus required is unfortunately often so highly priced that it is beyond the reach of many laboratories.

In the present study, attention was therefore directed to gas chromatography which showed promise of providing a relatively simple and inexpensive means of analysing gas mixtures.

Gas Chromatography.

Although gas chromatography is a comparatively recent development, an extensive literature already exists on the subject, but this is largely confined to the analysis of substances (or mixtures of these) that have boiling points above 0°C. Only a few investigators have reported results of the application of this technique to the analysis of permanent (or substantially permanent gases) such as those that are normally analysed by the chemical volumetric methods.

Janak⁴⁾ and Hrapia and Könnecke⁵⁾ used columns of activated carbon for permanent gases^{*} and silica gel columns for hydrocarbons. Carbon dioxide was used as carrier gas in both cases. Natural gas coke oven gas and water gas were analysed.

Coates and Brønner⁶⁾ used a stainless steel tube packed with silica gel for the separation of hydrocarbons up to propane and a liquid partition column for the heavier hydrocarbons.

Green, Moberg and Wilson⁷⁾ used a column packed with activated carbon for the analysis of mixtures of gases such as hydrogen, carbon monoxide, air, methane, carbon dioxide, ethane and ethylene. The temperature of the column was raised slowly during the analysis.

Patton/.....4.

* For convenience, the term "permanent" will be used for hydrogen, nitrogen, carbon monoxide and methane.

Patton, Lewis and Kaye⁸⁾ analysed similar mixtures using a column packed with activated carbon maintained at 180°C.

Ray⁹⁾ describes a method of separation of the lighter gases on a carbon column and heavier gases such as C₃ and C₄ hydrocarbons on a liquid partition column.

Kyryacos, and Boord¹⁰⁾ used a molecular sieve (Zeolite) column maintained at 100°C and helium as carrier gas to separate hydrogen, nitrogen, oxygen, methane and carbon monoxide. The time taken for an analysis was 24 minutes.

Janak¹¹⁾ analysed similar gas mixtures on a 15 ml. column with the same type of packing. He used hydrogen as carrier gas and maintained the column at minus 78°C. (Analysis time 5 minutes).

These papers suggest that the time taken for an analysis varies from about 5 minutes (for the determination of hydrogen, nitrogen, carbon monoxide and methane to 50 or 60 minutes for a complete analysis of a mixture containing all the commonly encountered components from hydrogen to C₄ or C₅ hydrocarbons.

The separating efficiency of a column is determined by two parameters: the number of theoretical plates and the separation factor. These parameters are functions of a number of controllable experimental conditions (e.g. type of packing, temperature and length of column, rate of flow of carrier gas) and the nature of the gases or vapours to be separated.

Thus in the case of a mixture of carbon monoxide and nitrogen the separation on a carbon column can be improved, (e.g. by increasing the length of the column, by reducing the rate of flow of the carrier gas and the temperature or by the

choice of/.....5.

choice of a more suitable activated carbon), from an overlap of the chromatogram to a period between the elution of these gases of three minutes or more.

The object of such modifications should be to effect complete separation between the components of the mixture that are most difficult to separate without increasing the period between the elution of any two components of the mixture so much that the time required for the complete analysis will be increased unduly.

The Detection of the Gases.

Assuming complete separation between the components of a mixture of gases, the quantitative error involved in the analysis is determined by the accuracy of detection, the recording and the interpretation of the chromatograms produced. The issue may be complicated by the fact that the components must be detected and measured while more or less diluted by the carrier gas.

Various detectors¹²⁾ have been developed but attention may here be confined to the Thermal Conductivity Cell and the Nitrometer Detector.

The Thermal Conductivity Cell.

This is probably the most widely used detector in gas chromatography. The sensitivity of this type of detector is high. Thus a full scale deflection on a recording potentiometer can be obtained by 0.1 mg. of the lighter gases and 10 to 20 mg. of substances boiling in the range 100°C to 200°C.¹³⁾

The instrument is of the differentiating type i.e. it produces a peaked rather than a stepped chromatogram and this is rather undesirable for quantitative work. The area under the peak/.....6.

the peak produced by a component is nearly proportional to the amount of the component present in the gas. For quantitative work this area has to be calibrated accurately by passing carrier gas containing known quantities of the components to be expected through the cell.

By using the internal normalisation technique calibration becomes unnecessary and it also obviates the necessity of controlling accurately the temperature and the gas flow rate from one analysis to another. However, a certain loss of accuracy is suffered by adopting this procedure because the area under the peak is a function of the concentration as well as the nature of the gas. The response of the detector is dependent on various factors which require close control during operation. Such factors are: the filament heating current and the temperature of the cell and that of the column. Errors are mainly due to the instability of the detector and to area interpretation and measurement, especially under skew and trailing peaks.

Since the application of gas chromatography to quantitative gas analysis is relatively new, the reproducibility and accuracy of the method are not yet well established. Using the thermal conductivity detector Paton, Lewis and Kaye⁸⁾ report an accuracy of plus/minus 1% to plus/minus 2% for C₃ and C₄ hydrocarbons. Green, Moberg and Wilson⁷⁾ were able to reproduce the analysis of hydrocarbon vapours with a precision of 2%.

Better results are said to be obtainable with commercial apparatus. Phillips⁴⁾ refers to a series of tests done on such an instrument. The maximum deviation between duplicate analyses was reported to be about 0.6% and the

deviation of/.....7.

deviation of the average of determined results from the amount present in the mixture was in no case higher than 0.2%.

Ray obtained a reproducibility of better than 1% on mixtures of light gases and hydrocarbon vapours.

The Nitrometer Detector.

Janak⁴⁾ introduced the use of carbon dioxide as carrier gas and collected the gas eluted in a nitrometer filled with concentrated potassium hydroxide solution, thus eliminating the carrier gas before the volume of the eluted gas was determined.

The nitrometer detector is less sensitive than the thermal conductivity detector but it has a number of practical advantages e.g.:

1. Compared with that of a thermal conductivity cell and ancilliary apparatus its cost is negligible.
2. It is insensitive to carrier gas flow rate and does not require accurate temperature control.
3. It is not affected by changes in the activity of the column packing, hence the temperature and other factors which influence the activity of the packing can be varied during the course of an analysis.
4. The chromatograms are of the integrated (or stepped) type. The apparatus requires no calibration and no extensive calculations are necessary as the volumes of the components are read off directly on the burette scale.
5. Eluted fractions, required for further analysis can easily be collected in separate burettes.
6. Automatic recorders have been developed^{4,15,16)} that can be used with this type of detector if desired.

The nitrometer method is limited to the analysis

of gases/.....8.

of gases and vapours that are not attacked by alkali and which do not condense (Acetylene is the only component possibly present in the types of industrial gases with which this investigation is concerned that is reported to be absorbed by alkali¹¹⁾).

Trace quantities cannot be detected with the nitrometer. (This is also a deficiency of the thermal conductivity detector¹²⁾). It can be remedied to some extent by increasing the size of the sample but care must be taken not to overload the column.

The accuracy and the precision of this method are dependent only on the error involved in reading the burette. Hrapia analysed samples by both the chemical volumetric and gas chromatographic methods. He reported that the agreement between the results obtained by the two methods was not very good the largest discrepancies being obtained for the hydrocarbons. The maximum error in reproducibility in the chromatographic analysis was, however, only 0.1%.

The Development of an Apparatus for Routine Analyses.

When considering the design of a practical apparatus for the routine analyses of industrial gases containing any or all of the following components: Carbon dioxide, oxygen, nitrogen, carbon monoxide, hydrogen, unsaturated and saturated hydrocarbons up to say C₂, the following matters were considered:

1. Since oxygen, nitrogen and carbon monoxide are eluted very nearly at the same rates it would be practically impossible to obtain a sharp separation between them in a column of simple design.

2. The direct/.....9.

2. The direct determination of nitrogen would be a distinct advantage.
3. As noble gases are expensive and not readily obtainable in South Africa, their use as carrier gas in routine analysis is ruled out.
4. Hydrogen and carbon dioxide are important components of most of the gas mixtures under consideration and their direct determination is desirable. If either were used as carrier gas its concentration in the gas sample should be determinable directly by other means. From this point of view, preference should be given to carbon dioxide as carrier gas as it can be accurately determined by chemical-volumetric analysis.
5. The choice of carbon dioxide would allow one to use Janak's nitrometer detector technique, provided that carbon dioxide of high purity could be obtained.

Provision of Pure Carbon Dioxide.

After some preliminary experiments the preparation of carbon dioxide (in the quantities required) by interaction of carbonates and acids was abandoned as impracticable for the present purpose. The available compressed carbon dioxide was found to be too impure to serve as carrier gas.

Sufficiently pure carbon dioxide was obtained from commercial solid carbon dioxide (dry ice) by adopting the following procedure:

The dry ice was ground to a fine powder and charged to a glass container. The container was left open for an hour or more to allow the entrapped air to escape freely with the carbon dioxide evolved.

After about/.....10.

After about one hour, the carbon dioxide issuing from the container was so pure, that only minute bubbles rose in the nitrometer tube. Blank determinations indicated that about 0.02 cc. of impurity collected in the nitrometer tube per hour. One hundred gram of dry ice is sufficient for about 24 hours operation.

Control of the Rate of Flow on the Carbon Dioxide.

The most satisfactory control of the rate of gas flow was obtained by fitting a small electric heater^{*} in the dry ice container and by placing this container in a mixture of dry ice and alcohol whereby (with the heater off) the vapour pressure of the carbon dioxide above the dry ice in the vessel was reduced to about atmospheric pressure (this part of the apparatus is shown in the sketch Fig.1.)

The rate of flow of the gas could then be controlled closely by regulating the current passing through the heater (manipulation of a variac transformer or a rheostat).

The apparatus can be adapted to automatic flow control by using relays, actuated by contactors fitted to a manometer or flow meter, to control the heater current.

Preparation of Gas Mixtures.

Having chosen carbon dioxide as carrier gas it was decided to determine the carbon dioxide content of gas mixtures before the chromatographic analysis by the conventional chemical volumetric technique. To simplify the chromatographic analysis it was considered advisable to provide also for the chemical volumetric determination of oxygen.

The chromatographic/.....11.

* 0.5 to 45.0 Watt delivers a gas flow of about 0.2 to 6 l/h.

The chromatographic separation would then be confined to the gases: hydrogen, carbon monoxide, nitrogen, methane, ethane, ethylene etc.

In order to ensure accurate recording by the nitrometer it would be desirable to develop a column and operating technique whereby an interval of one to two minutes between the complete elution of any one component and the appearance of the next component could be ensured, without extending this period unduly for some of the other components.

For such development work and in order to determine the accuracy of determinations, it was considered desirable to have available pure gases and mixtures of known composition.

The following gases were therefore specially prepared as they were not readily available in the pure state:

- Carbon Dioxide: By reaction of sodium bicarbonate with sulphuric acid.
- Carbon Monoxide: By reaction of formic acid with sulphuric acid.
- Oxygen : By thermal decomposition of potassium permanganate at 400°C.
- Methane : By reduction of methyl iodide over aluminium amalgam in the presence of methyl alcohol.
- Ethane : By reduction of Ethyl iodide over the same amalgam in the presence of ethyl alcohol.
- Ethylene : By reaction of methyl alcohol with anhydrous ortho phosphoric acid at about 200°C.

The crude gases were separated from impurities by freezing out or fractional distillation using liquid oxygen or a suitable freezing mixture. (details of the techniques adopted

are provided in the Fuel Research Institute Technical Memorandum No. 17 of 1957.)

The analyses reported later in this paper were all done on "synthetic" mixtures of these pure gases.

Development of Chromatographic Columns.

The columns were made from 7 mm bore tubing. In order to reduce the size of the apparatus it was considered advisable to bend the tubes in the form of a spiral. Such columns were found unsatisfactory however and the idea was abandoned. The tubes were then bent in the form of a U or W and this was found satisfactory. Four-way stopcocks of the type used in some Orsat gas analyses catalyst tubes were fitted to the ends of these tubes, (for details of this type of stopcock see the detail of the gas pipette Fig. 1 (a)).

Absorbents.

Four types of activated carbon were available. Type A was a granular form (-20 to + 50 mesh) and the types B, C and D were in wire form (1 mm diameter by 1 to 2 mm long).

The absorbent was charged to the tubes and lightly compacted by slight shaking and tapping. The column was then evacuated while being heated to about 400°C. It was then allowed to cool down while maintaining the pure carbon dioxide current until the absorbent was again at room temperature.

Other columns were filled with silica gel. These were then heated to about 180°C while a stream of carbon dioxide was passed through. After about one hour the column was allowed to cool while carbon dioxide was still passed through until the column had attained room temperature.

The Separation of Carbon Monoxide and Nitrogen.

It was established in preliminary experiments that among the gases considered, the separation of carbon monoxide and nitrogen presented the greatest difficulty.

As shown in Table 1 (experiments 1 to 3) good separation between these gases was not obtained with carbon A even when the length of the column was extended to 3.6 m.

With Carbon C good separation was obtained using a 3.6 m. column but the interval between the elution of carbon monoxide and methane was very long (exp. 5 Table 1). This difficulty could be overcome by heating the column to 120°C after the emergence of the carbon monoxide (exp.6). This procedure has the disadvantage that the column must be cooled down before the next analysis can be started.

Carbon D yielded more satisfactory results at 20°C (exp.7) for the separation of hydrogen, nitrogen, carbon monoxide and methane. It could be used at elevated temperature for separating hydrocarbons but if operated throughout at the higher temperature, the resolution of nitrogen and carbon monoxide was adversely affected.

Operation with more than one Column.

Attention was therefore directed to a preliminary separation of the permanent gases from the higher hydrocarbons. The permanent gases could subsequently be separated on a long charcoal column under suitable conditions and the hydrocarbons on a silica gel column or a short carbon column.

The apparatus was arranged so that the columns could be either connected in series or operated separately i.e. any column could be isolated by suitable manipulation of the stop-cocks.

This procedure would work satisfactorily if the interval between the elution of methane and the following hydrocarbon from the first column could be made large enough so that there would be absolute certainty of transferring all the methane to the second column without allowing any of the higher hydrocarbons to enter it.

Silica gel has properties that make it superior to activated carbon for the chromatographic separation of the higher hydrocarbon gases. Unfortunately it was not possible to increase the interval between the elution of methane and ethane on this column much above 2 minutes (expts. 9 and 10).

Although such an interval is adequate for an experienced operator to effect the manipulations required when using a 2-column analysis apparatus, it was considered to be too short for practical purposes.

When using a short carbon column (carbon D) maintained at 110°C, this interval could be increased to as much as 14 minutes and this column could also be used for the separation of higher hydrocarbons.

A combination of a short, heated carbon column and a long carbon column maintained at room temperature (for separating the permanent gases) this provides one solution to the problem of devising a practical analysis apparatus.

The activated carbon has limitations in regard to the separation of hydrocarbons in the range C₄ and C₅ and therefore another alternative was investigated.

It was found that the short column filled with the active carbon D and maintained at room temperature retained the hydrocarbon gases for about 100 minutes while the permanent gases were fully eluted within about 5 minutes (Experiment 12). Such a carbon column could be used for eliminating the heavier hydrocarbon gases from about 10 consecutive samples of gas before it was necessary to remove the hydrocarbons retained in it (by heating the column while passing carbon dioxide through it).

This fact was made use of in an alternative arrangement in which three columns were used. The analysis was done on two samples. One sample was passed into a short carbon column for the elimination of the hydrocarbons. The eluted permanent gases were separated on a long carbon column. The second sample was passed through a silica gel column where permanent gases were eluted as a group but excellent separation of hydrocarbon gases up to C₅ was obtained.

By adopting this arrangement the time required for a complete analysis could be reduced to 45 minutes.

The results of analyses of synthetic gas mixtures obtained with the column combinations numbered Exp. 13, 14 and 15 in Table 1 are given in Table 2. This table also contains results of Orsat analyses on the same sample. These results are the average of at least three analyses.

An analyst with 3 years experience performed the analysis on the Orsat apparatus. The chromatographic analyses

were made by/.....16.

were made by two operators, one with about eight months experience and the other with about a week's training. The latter was able to reproduce the results of the experienced operator to within 1%. The time required to train personnel to operate a chemical volumetric apparatus is usually much longer.

The results obtained when using the different chromatographic columns agree to within 1%, and are in agreement with the amounts present. The results obtained for nitrogen and methane with the Orsat analyser do not agree with the values obtained by the chromatographic method, but the latter are more reliable. The time for a complete analysis on the Orsat apparatus is two hours, whereas the same analysis can be done by the proposed technique in less than an hour including the time required for the determination of carbon dioxide and oxygen by chemical means. With experience this period can be reduced by increasing the carrier flow rate or the column temperature at some stage of the experiment but such manipulation is not advised until the operator has adequate experience.

To illustrate the insensitivity of the nitrometer detector to variation in experimental condition during an analysis some typical results obtained during the course of this investigation are given in Table 3. They represent the average values of at least two analyses of the same gas mixture. In experiment numbers 1, 2 and 3, the same gas sample was analysed at different carrier flow rates. In Experiments 1 and 3 the rate was held constant at 2.5 and 3.5 l/h respectively while the rate was changed from 1.5 to 5.5 l/hr during the course of the analysis in Experiment 3.

Experiments 4 and 5 refer to the analysis of another gas sample. In experiment 4 the column temperature was maintained at 20°C while in experiment 5 the temperature was raised from 20°C to 120°C after elution of carbon monoxide. Although the conditions were varied considerably during these experiments, the standard deviation (from the average) between individual determinations did not exceed 0.6%.

Automatic Recording of Components.

The nitrometer recorder can be adapted quite easily to automatic recording of the gases eluted from the column.

A simple automatic recorder was developed during the course of this study and is described in the Fuel Research Institute Technical Memorandum No. 16 of 1957. Figure 2 represents a typical chromatogram obtained with this apparatus.

Although the results shown in Table 2 prove that the nitrometer recorder can be operated very well without such a refinement, the automatic recorder has distinct advantages. It provides a more exact and permanent record of the analysis especially in some cases where froth formation at the meniscus in the nitrometer (due to micro bubbles) renders accurate direct readings of the actual volume somewhat difficult.

The Apparatus and Its Operation.

One arrangement of the apparatus is shown schematically in Fig.1.

Before any test the apparatus from I over D to the nitrometer is flushed with carbon dioxide.

I is the carrier gas generator filled with solid carbon dioxide and provided with a small electric heater. The gas flow is determined by flow meter J.

A comparatively large sample of the gas to be analysed is transferred (via a drying agent if it should be moist) to the gas burette A which has mercury as confining liquid and a compensating tube as shown.

This sample is then analysed by the conventional chemical absorption methods for carbon dioxide and oxygen by passing it successively into the suitably charged absorption pipettes B1 and B2. The gas will rather lose than gain moisture in this process.

The residual gas from these determinations is now transferred to the receiver C where it is stored over mercury. If desired another sample of gas can now be drawn into the burette for preliminary analysis.

A portion of the residual gas is transferred to the sample pipette D (shown in greater detail in the inset Fig. 1 (a)) (capacity 3.5 ml) by the following procedure. The pipette is isolated from the carrier gas stream and connected to the storage vessel C and the manifold (up to stopcock K) by manipulation of the stopcocks. The pressure in C is then increased by raising the levelling bulb. By opening K momentarily to the atmosphere the pipette is flushed with the gas sample. The pressure is then restored to atmospheric pressure. The pipette is then isolated from the storage vessel and the manifold by means of the lower pipette stopcock. By manipulation of the upper stopcock, the sample in the

pipette is flushed by the carrier gas into the absorption columns.

The columns E, F and G are respectively the short carbon column, the silica gel column and the long carbon column. The operating details for the three column arrangements finally investigated are given below.

(1) Silica gel and Long Carbon Column. Exp.(13).

The permanent gases pass through the silica gel column (F) without appreciable separation and at a flow rate of 1.5 l/hr., all these gases will have entered the column G within 5 minutes of the flushing of the pipette. After 6 minutes the column F is isolated and the carrier gas is made to pass directly into G. In order to isolate the column F at the correct time (which must be determined in a preliminary experiments) it is necessary to control the gas flow accurately.

Hydrogen was found to appear in the nitrometer within about 5 minutes from the time of flushing D and the methane was fully eluted from G after 25 minutes. At this stage column G is isolated from the system and the carbon dioxide is again made to pass through the silica gel. The elution of all the hydrocarbon gases was complete within 15 minutes of bringing F into the circuit again. The time taken for the complete analysis is about 45 minutes. The only disadvantage of this procedure is that it requires close control of the carrier flow rate until the preliminary separation between the permanent gases and hydrocarbons is effected.

(2) Short Carbon Column (at 110°C) and a Long Carbon Column.
Exp.(14)

The procedure is essentially the same as for the silica gel - carbon column combination described above. The time interval between the elution of the permanent gases and the first hydrocarbon on the short column is long enough to make close control of the carrier gas flow rate unnecessary. The retention times of the hydrocarbons are rather long on this column as compared with the retention times on silica gel.

It is possible to control the temperature of this column (up to 450°C) by inserting it through a hole in a stopper which is fitted to a Dewar flask. A 450 watt heater (of the type fitted to household radiators) is placed in the flask. The current through the heater is controlled by a variac transformer. Since the temperature of the column is not critical, no automatic temperature control device is required.

(3) Short Carbon Column, Silica gel and a Long Carbon Column.
Exp.(15)

The silica gel column (F) is first isolated, and the carrier gas is made to pass through the two carbon columns. After 5 minutes the permanent gases have passed through the short column which is then isolated. (The hydrocarbons are retained on the short column). The permanent gases are then separated on the long column. The hydrocarbons are finally determined on a separate sample on the silica gel column while the two carbon columns are isolated.

A record must be/.....21.

A record must be kept of the time that the carrier gas is made to pass through the short column so that it can be cleaned up before any of the accumulated hydrocarbons may be eluted with the permanent gases. It is of course necessary to know the retention times of the first hydrocarbon in order to calculate the time that the column can be used with safety.

The carbon D packed in this column could be used for about ten determinations at a carrier flow rate of 2 l/h. It is convenient to clean the carbon at the end of each day's work. The column is strongly heated for about 15 minutes with a brush flame while carbon dioxide is passed through the column. Since, with the type of gas generator used, the gas cannot be turned off, it can be allowed to pass through the column while it is cooling off overnight.

From a practical point of view all three of the tested combinations yield good results. However, the three-column combination is preferred since the method requires no critical gas flow control or high temperature column.

Conclusions.

The quantitative accuracy attainable with the technique developed is superior to that obtainable with the Orsat gas analysis apparatus especially with the hydrocarbon components.

The time required for an analysis was found to be shorter by this technique and the operators required much less time to produce reliable results.

Comparing the accuracy figures determined in this investigation with published results in which a thermal

conductivity cell detector was used, it is concluded that the nitrometer detector yielded at least as good results as the latter.

The cost of the whole apparatus is so low that it could be acquired by any laboratory doing routine analyses.

The results have shown that the active carbon used should be chosen with care to ensure optimum results.

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T A B L E 1.

Experiment Number	Columns		Flow Rate l/h.	Analysis Time (Minutes)	Interval between Neighbouring Components (Minutes)					
	Length (M)	Temp. °C			Packing.	H ₂ - N ₂	N ₂ - CO	CO - CH ₄	CH ₄ - C ₂ H ₆	C ₂ H ₆ - C ₂ H ₄
1	1.8	20	1.5	21	1	0	5	-	-	
2	2.7	20	1.5	25	3	0	5	-	-	
3	3.6	20	2.0	27	4	0	15	-	-	
4	2.7	20	1.5	21	-	0.25	-	-	-	
5	3.6	20	1.5	70	7	3	23	-	-	
6	"	20 & 120	1.6 Ca	39	4	2	10	-	-	
7	"	20	2.0	24	2	1	7	-	-	
8	"	180	2.0	80	2	1	2	22	4 *	
9	0.6	20	1.5	15	0.5	0	0	2.	3.5	
10	0.9	20	1.5	23	1.0	-	-	2.5	4	
11	0.45	110	1.5	53	1.0	0	0	14	3 *	
12	0.45	20	1.5	-	1.0	0	0	retained for 100 min.		
13	(i) 0.6 (ii) 3.6	20 20	1.5- 2.0	45	2	1	7	2.	3.5	
14	(i) 0.45 (ii) 3.6	110 20	1.5 - 2.0	60 Ca	2	(ii) 1	7	(i) 14	3 *	
15	(i) 0.45 (ii) 3.6 (iii) 0.6	20 20 20	1.5 - 2.0	45	2	(i) & (ii) 1	7	2.	(iii) 3.5	

TABLE 1. Time interval between elution of components on various columns and experimental conditions.

* The elution sequence of ethane and ethylene is reversed on carbon columns.

T A B L E 2.

Vol. %	Chromatographic Column Combination.			Orsat Analysis	Amount Present.
	Exp.13	Exp.14	Exp.15		
CO ₂	0.0	0.0	0.0	0.1	0.0
O ₂	9.1	9.4	9.4	8.4	8.9
H ₂	18.6	18.7	18.6	18.5	18.6
N ₂	34.8	34.0	34.6	33.0	34.8
CO	17.2	17.1	17.6	17.9	17.3
CH ₄	2.7	2.7	2.7	4.2	2.8
C ₂ H ₄	16.0	16.5	16.0	16.9	16.1
C ₂ H ₆	1.6	1.6	1.5	1.0	1.5
Time Required for Analysis	45 min.	60 min.	45 min.	2 hours	

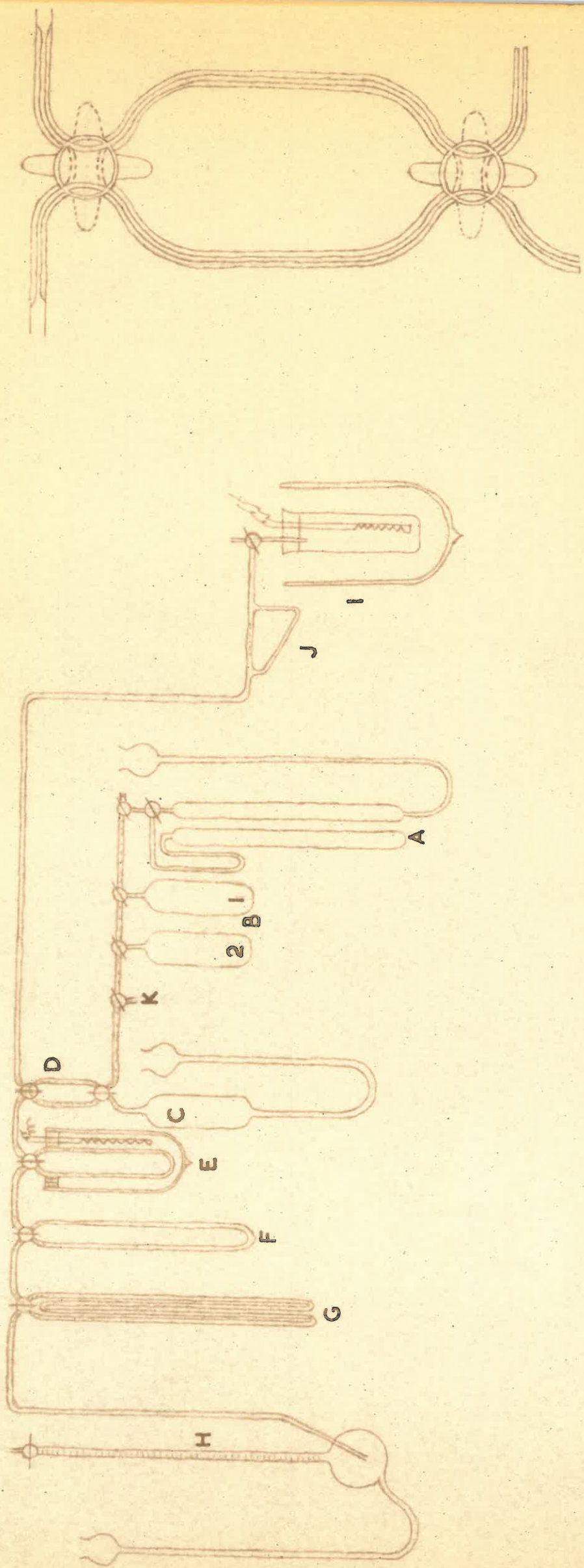
T A B L E 2.

Results of analyses of Standard sample by three different column combinations and by chemical volumetric analyses.

T A B L E 3.

Experiment Number.	Column Temperature °C.	Flow Rate l/h.	Average Analyses.			
			% H ₂	% N ₂	% CO	% CH ₄
1	20	3.5	15.63	36.39	23.18	24.8
2	20	1.5 - 3.5	15.63	36.66	23.72	23.99
3	20	1.5	15.63	36.66	23.72	23.9
4	20	2.0	9.6	21.0	55.5	13.9
5	20 - 120	Ca. 1.8	9.7	21.4	55.9	13.1

TABLE 3: Summary of results obtained by variation of experimental conditions during the course of an analysis.



(a)

FIGURE 1. DIAGRAM OF GAS ANALYSIS APPARATUS
 (a) DETAILS OF SAMPLING PIPETTE.

TIME IN MINUTES.

20

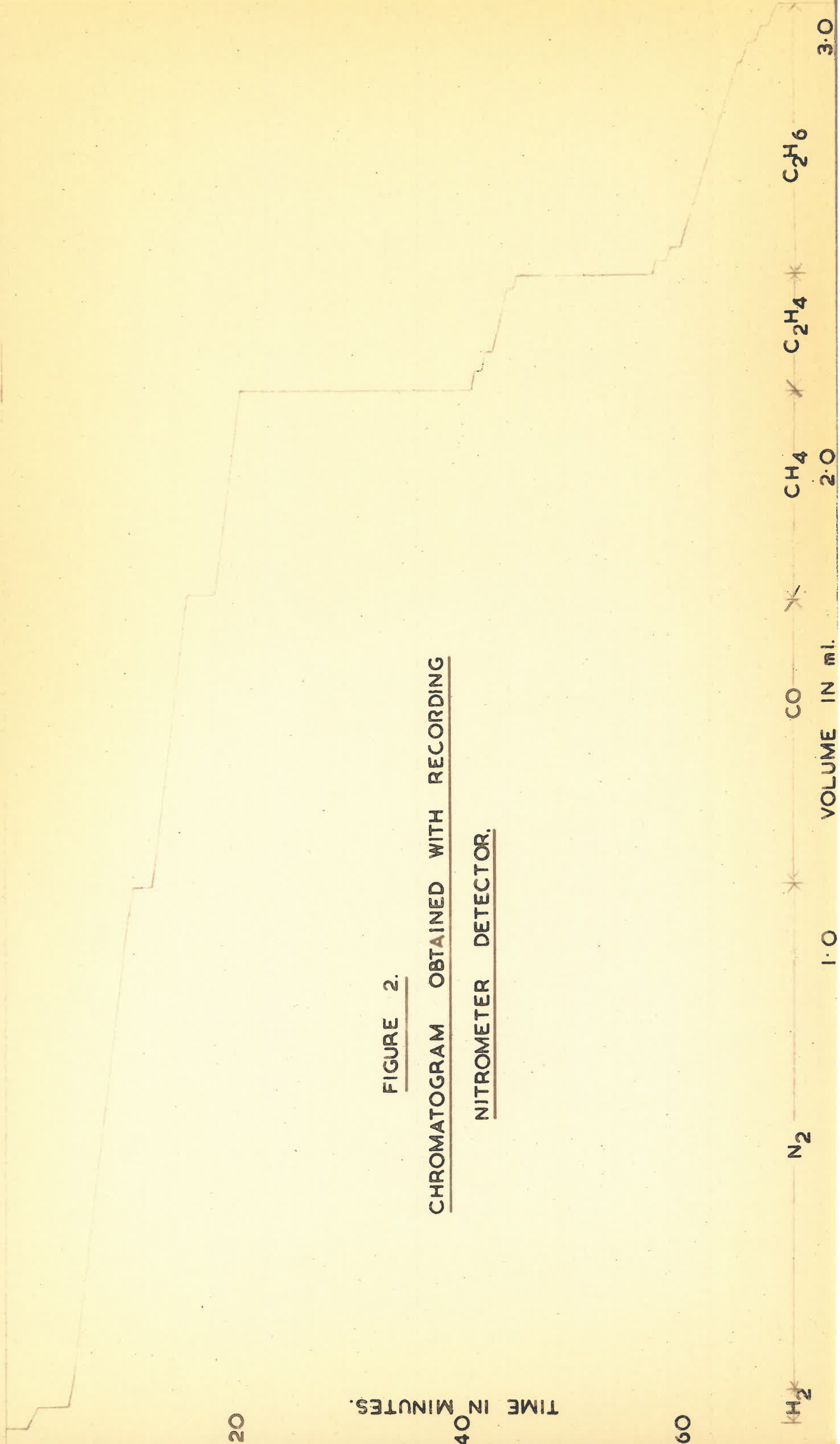
40

60

FIGURE 2.

CHROMATOGRAM OBTAINED WITH RECORDING

NITROMETER DETECTOR.



H₂*

N₂

1.0

CO

CH₄

C₂H₄*

C₂H₆

VOLUME IN ml.

2.0

1.0

3.0

