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DEPARTMENT OF MINES AND TECHNICAL SURVEYS

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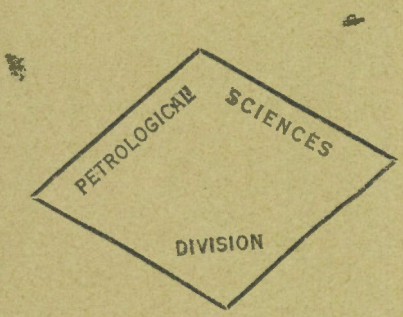

FIELD AND LABORATORY METHODS USED BY
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No. 6

DETERMINATION OF HYDROCARBONS IN SOILS BY GAS CHROMATOGRAPHY

(Report and 2 figures)

A. H. Debnam

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ABSTRACT

The following is a method of determining light hydrocarbons in soil by gas chromatography. To prepare the sample the soil is dried at 110°C, lightly crushed and sieved through a 200 mesh Tyler screen. A weighed portion of the minus 200 mesh fraction is placed in a reaction flask and the system evacuated.

The sample is heated after addition of 2N hydrochloric acid and the evolved gas passed through a series of traps to remove CO_2 and moisture. The hydrocarbons are finally removed in a trap immersed in liquid nitrogen.

The last trap is removed from the system, brought to room temperature, and attached to a gas chromatograph. The gas mixture is flushed into the instrument, the hydrocarbon components separated, and determined quantitatively by means of a hydrogen flame ionization detector.

Fourteen or fifteen samples may be processed per 8-hour day with a precision of $\pm$ 10 per cent.

Field and Laboratory Methods used by the

Geological Survey of Canada in Geochemical Surveys

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DETERMINATION OF HYDROCARBONS IN SOILS BY GAS CHROMATOGRAPHY

INTRODUCTION

The procedures[1] described in this paper were developed by the writer during the tenure of a National Research Council of Canada post-doctorate fellowship from March 1961 to November 1962. A later publication will describe field procedures and the results obtained from tests over known oil and gas fields in Canada.

The aim of the project was to determine whether the techniques of geochemical prospecting could be applied in the search for oil and gas in Canada where surficial glacial deposits and high organic content in the sedimentary column are common complicating factors.

The author is grateful to the National Research Council of Canada for granting him a fellowship and to the Geological Survey of Canada for the use of laboratories and equipment in Ottawa and for making available personnel and equipment in the field.

GAS CHROMATOGRAPHY

Geochemical prospecting for petroleum and natural gas received considerable attention during the period 1935-1945, in both the U.S.A. and U.S.S.R., and many methods were developed. Those with the greatest merit involved the detection of the light saturated hydrocarbons in surface soils, but unfortunately the laboratory determination of extremely small amounts of hydrocarbons required a complicated apparatus and skilled operators.

Recent advances in the use of gas chromatography for organic analysis now give the analyst a technique with these advantages: low cost, simplicity, high sensitivity, good quantitative accuracy with small sample quantities, little or no interference between components, ease of data interpretation, and a permanent record of results.

As most readers will not be familiar with gas chromatographic techniques they will be discussed briefly before the analytical procedures are described in detail. For a more complete treatment, see the various monographs and papers mentioned below.

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[1] Canadian Patent Application 863, 197.

Desty and Harbourn (1957)[1], Keulemans (1959), and Phillips (1956) have discussed gas chromatography in detail. Shorter reviews have been prepared by Harris (1959), Rose (1959), Dal Nogare (1960), and McWilliam (1961). Interesting general papers, some written specifically for those unaquainted with the subject, are by Hausdorff and Brenner (1958 a-d), Locke (1958), Askins (1959), Knox (1960), Keller (1961) and Pecsok (1961).

Since its introduction by James and Martin (1952 a, b), gas chromatography has revolutionized research in organic chemistry. It is a special branch of chromatography, which is a physical method of separating materials from one another where one phase is stationary and the other is mobile. If a gas is the mobile phase the method is termed "gas chromatography". This includes (a) gas-solid or adsorption chromatography when the stationary phase is a solid, and (b) gas-liquid chromatography when the stationary phase is a liquid supported on a solid. The separation is carried out in a column of stainless-steel, copper or glass tubing in which the stationary phase is packed, and through which an inert carrier gas is continuously passed. The sample to be analyzed is introduced at the inlet of the column and emerges at the outlet as completely separated individual components. A detector and recorder system make possible the quantitative estimation of the components. Under ideal conditions each component emerges at a different time as a very narrow band. Such conditions may be difficult to achieve and several compromises of the variable parameters in the system may have to be made.

The following is a brief description of the operation of the column. As the sample is moved through the column by the carrier gas the partitioner (column packing) interferes in a selective manner with the progress of each compound present, slowing up the progress of some and letting others through the column more swiftly. The sample can be considered as a plug of molecules injected into the carrier gas at the inlet to the column. Some of the molecules rapidly dissolve in or are adsorbed by the partitioner and a dynamic equilibrium is soon established as they pass back and forth between the partitioner and the vapour filling the interstices of the column packing. The more volatile molecules are continuously being swept to the head of the plug where they are redissolved or readsorbed; the less volatile molecules fall to the tail of the plug, but they too are continuously being picked up and inched forward by the gas stream pressing from behind. Eventually, under suitable conditions, all the molecules of the more volatile components are carried well ahead of those of the less volatile components and a clean separation is achieved. (Terms such as "distribution coefficients" and "theoretical plates" which are commonly used in discussing gas chromatography have been avoided here. A more technical explanation of column operation may be obtained from the literature cited earlier.)

The variable parameters that determine the success or failure of a particular analysis are (1) carrier gas, (2) column packing

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[1] Dates in parentheses refer to publications in the Selected Bibliography.

(partitioner) and temperature, (3) length and diameter of column, (4) detector, and (5) recorder. Each of these variables is discussed in more detail below.

1. Carrier Gas. The variables that must be considered are the type of gas, the flow rate, and the pressure. These have been discussed by Hausdorff and Brenner (1958b, 1958c). Whereas certain radioactive detectors require specific carrier gases the hydrogen-flame detector used for the determination of light hydrocarbons can accommodate any gas that is hydrocarbon-free, e.g. helium, nitrogen, argon, or air. The flow rate is usually between 20 and 100 mls per minute at a pressure of 30 to 45 pounds per square inch. Flow rate and pressure are best determined by trial and error for each column used.

2. Column Packing and Temperature. The partitioner largely determines the performance of the chromatograph, because one that works well with one type of sample may be completely useless for another type. Detailed discussions of column packings have been given by Hausdorff and Brenner (1958a, 1958b, 1958c).

The partitioner must not react with the sample being analyzed nor must it be volatilized by the stream of carrier gas that propels the sample through the column. The latter condition is a function of column temperature, and all liquid partitioners have a maximum temperature above which they must not be used. This may be as low as room temperature (e.g. propylene carbonate) or as high as 400°C for certain high-temperature packings. In general the solid adsorbants such as silica gel and alumina are not affected by high temperatures.

A great variety of partitioners have been used for light hydrocarbon analysis. They include hexamethyl-phosphoramide (Askins, 1959; Favre, Hines, and Smith, 1958; Locke, 1958), dimethyl sulfolane and hexadecane (Locke, 1958), glutaronitrile and propylene carbonate (McKenna and Idleman, 1959) and silica gel and alumina (Greene and Pust, 1957; Scott, 1959; McKenna and Idleman, 1960).

The particle diameter of the packing is important as it affects eddy diffusion and back-pressure in the column. In general material of about 50 mesh is favoured.

3. Length and Diameter of Column. The degree of resolution of the components of a mixture is proportional to the square root of the column length, making long columns undesirable. Convenient lengths are from 3 to 10 feet. Increasing the column diameter decreases the degree of resolution. Packed columns of internal diameter 1/8 to 1/4 inch are generally the most suitable.

4. Detectors. The detector is located at the outlet of the column to signal the emergence of each different component. It does not identify the component but merely indicates when the output gas is carrying foreign molecules. Identification of the components is made possible by the determination of elution times. For example, if temperature and other conditions are kept constant for each analysis

a sample of pure ethane and the ethane component of a mixture of unknown gases will elute from the column outlet in the same interval of time after sample injection at the column inlet. Many different types of detectors are available, and these have been discussed and compared by Hausdorff and Brenner (1958b) and McWilliam (1959). Due to their great sensitivity, the ionization detectors are the most important in the present project. Lovelock (1961) has discussed in detail the numerous types. In particular the hydrogen flame ionization detector has been fully described by McWilliam and Dewar (1958). This is the most satisfactory detector for the low-molecular-weight hydrocarbons whereas certain radioactive ionization detectors exhibit extreme sensitivity for hydrocarbons of higher molecular weight. The hydrogen flame detector has the advantage of not responding to the fixed gases (nitrogen, oxygen, etc.), and it is insensitive to water and carbon dioxide.

5. Recorders. The recorder indicates the amount of material passing through the detector by converting the detector signals into a graph on chart paper (a chromatogram). Peak areas, rather than peak heights, provide quantitative data because they are less sensitive to variations in column temperatures. The recorders most commonly used in gas chromatography are potentiometric having a 1-millivolt range, a 1-second pen speed, and a 12-inch chart moving at a rate of 1/2 to 1 inch per minute. To relieve the analyst of area measurements, various automatic integrators are available (e.g. the ball and disc integrator).

Procedures

Either one of two important procedures may be used to achieve optimum separation of components in a wide boiling range mixture. These procedures are temperature programming and back-flushing.

Temperature Programming. Habgood and Harris (1960) and Emery and Koerner (1961) have used temperature programming as an analytical technique. When the components of a sample mixture have a wide boiling range (e.g. the paraffin hydrocarbons ethane, b.p. -89°C to n-pentane, b.p. +36°C) their separation is difficult to achieve under isothermal conditions. If a low column temperature is used the more volatile substances are resolved but the less volatile components lag behind and are spread out by diffusion, resulting in low wide peaks. Use of a high column temperature sharpens the peaks of the less volatile components, but the more volatile substances are poorly resolved. If, however, the temperature of the column is increased from a low to a high value at a uniform rate throughout the analysis (i.e. temperature programmed) it is possible to achieve optimum conditions for good resolution of both the low-boiling and the high-boiling components. The result is completion of a required analysis in a greatly reduced time, together with a considerable improvement in peak dimensions (narrow high peaks instead of broad low peaks). One disadvantage of temperature programming is that the column must be cooled to the initial temperature before the next analysis can be commenced.

Back-flushing. Favre, Hines and Smith (1958) have used this method for the analysis of natural gas. It finds greatest application for analyses in which results are required for only the low-boiling components; those for the less volatile substances can be disregarded, in fact they need not even be separated. To apply the procedure the analysis is commenced in the normal manner under isothermal conditions. When the components of interest have been eluted from the column the carrier-gas flow is reversed, causing the strongly retarded unwanted components remaining in the column to be swept back to the column inlet where they emerge as a single group to be detected as a single peak. The next sample can be injected immediately as the column is clear and its temperature has not changed.

LIGHT HYDROCARBON ANALYSIS BY GAS CHROMATOGRAPHY

Successful gas chromatography for any particular analysis requires the correct selection of each parameter from the multitude of available choices. In this project the controlling conditions were: (1) the determination of minute amounts (in the range of parts per billion in original soil sample) of hydrocarbon components, and (2) the completion by chromatographic analysis of a sample in 25 minutes or less to avoid accumulation of samples from the extraction apparatus. These conditions were fulfilled by the use of the hydrogen flame ionization detector and temperature programming respectively.

The gas chromatograph chosen for the project was the Burrell Kromo-Tog Ionization Model K-7. This instrument had a hydrogen flame detector together with an alternative thermionic emission ionization detector for versatility, and automatic temperature programming at rates up to 40°C per minute to a maximum of 400°C. No modifications to the instrument were necessary, but the sample plug supplied with the unit was replaced by a special manifold designed to accept the hydrocarbon trap from the extraction apparatus.

The carrier gas was helium flowing at 60 mls per minute at a pressure of 30 pounds per square inch. Columns were prepared from 1/8-inch internal diameter (3/16 inch O.D.) copper tubing with brass Swagelock fittings. Several different partitioners were tried under various conditions. The most suitable separations were achieved with a 4-foot column packed with 40-60 mesh activated alumina, temperature programmed from 100°C at the beginning of the analysis to 300°C maximum at a rate of 40°C per minute. This maximum temperature was maintained until all materials were eluted from the column. The components to be determined—ethane, propane, butanes and pentanes—were eluted in the first 5 minutes. Clearing the column took 9 minutes, and a further 9 minutes were required to cool the column to 100°C. The total time of 23 minutes was within the 25-minute limit specified previously; the extra 2 minutes were required for trap adjustments. Extremely good resolution of components and sharp peaks were features of the chromatograms obtained (Fig. 1).

Quantitative estimates were made by comparing peak areas from test samples with those given by known amounts of each component or those given by a standard natural gas sample.

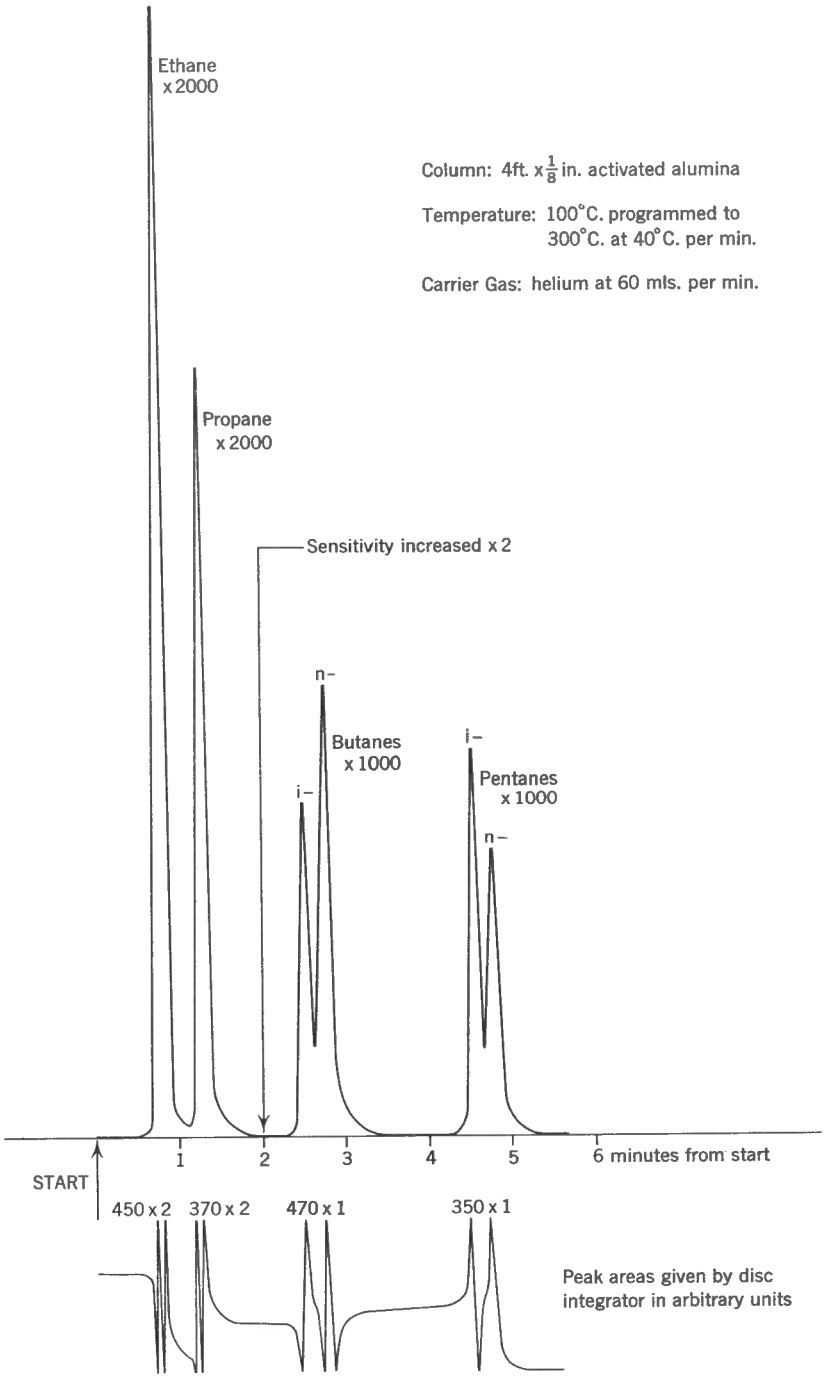

Figure 1. Chromatograph of soil hydrocarbons

Most commercial gas chromatographs do not incorporate automatic temperature programming. With these instruments alternative column packings, e.g. hexamethyl-phosphoramide, used in conjunction with isothermal operation and back-flushing should produce suitable results.

EQUIPMENT AND REAGENTS

Sample Preparation

1 oven, drying
3 dozen beakers, pyrex, 150-ml
3 dozen beakers, pyrex, 250-ml
1 pair tongs, oven
1 marker
1,000 envelopes, small, for sample storage
1 balance, laboratory
1 pestle and mortar, porcelain
1 set sieves, 8- or 10-inch brass; 20, 80 and 200 mesh
1 spatula

Reagents and Auxiliary Equipment

1 cylinder, graduated, 1,000-ml
1 cylinder, graduated, 500-ml
1 cylinder, graduated, 100-ml
1 bottle, 5-gallon
4 bottles, 1-gallon
2 flasks, pyrex, 1-litre, with rubber stoppers
1 still, water
4 gallons hydrochloric acid, A.C.S.
20 pounds potassium hydroxide pellets, A.C.S.
2 pounds magnesium perchlorate, A.C.S.
2 pounds Ascarite, 20 - 30 mesh

Extraction Apparatus and Accessories

30 feet alloy rod, 1/2-inch, for frame
3 dozen connectors, frame
1 dozen clamps, versatile, large
1 dozen clamps, versatile, medium
1 dozen clamps, versatile, small
1 dozen clamps, utility, various sizes
1 jack, or alternative arrangement for raising and lowering heater
1 heater, electrothermal, for 1-litre flask, with regulator
4 flasks, 1-litre
1 funnel, dropping, 250-ml
2 condensers
1 swan neck
1 splash head
8 stopcocks
2 stopcocks, 3-way
3 connectors

2 U-tubes
2 U-tube connectors
2 manometers, mercury
1 flask, filtering, 50-ml
2 flasks, filtering, 250-ml
4 joints, ball-and-socket, male
4 joints, ball-and-socket, female
4 clips
1 reservoir, 24-inch x 1 1/2-inch glass tube
1 pump, vacuum
3 feet tubing, pressure (pump to reservoir)
12 pounds tubing, glass, various sizes to 6 mm I.D.
30 feet tubing, rubber pressure, various sizes
30 feet tubing, tygon pressure, various sizes
2 dozen stoppers, rubber, Nos. 4, 5, 6, 7
1 pound beads, glass
3 flasks, Dewar, 1-litre
3 pinchcocks, hose
1 tester, vacuum
1 pair gloves, rubber
1 brush, bottle on wire, 4-inch x 1 1/2-inch diameter
8 ounces grease, silicone high vacuum
3 litres liquid nitrogen (daily supply)
1 tank, oxygen with regulator
1 torch, glass-blowing, for oxygen-gas
1 lighter, gas
1 pair glasses, glass-blower's
3 stands, iron
1 dozen clamps, iron, various sizes
6 clamp holders
1-pound rod, glass
1 pair scissors
5 dozen corks, bark, all sizes
1 set borers, cork
1 burner, gas
3 bottles, wash, polythene
3 dozen beakers, 800-ml
6 packets cleaning tissue

Gas Chromatograph and Accessories

1 gas chromatograph, complete (with automatic temperature programming or a back-flush arrangement and a suitable recorder with integrator, together with spare parts)
1 tank of helium
1 tank of hydrogen
1 tank of compressed air
3 regulators, pressure, for gas tanks
3 supports, gas tank
25 feet tubing, copper, 1/8-inch I.D., 3/16-inch O.D., for columns
4 dozen Swagelock brass fittings for 3/16-inch tube (nuts, ferrules, unions, etc.)
50 grams each of various column packings, including activated alumina, 40 - 60 mesh

1 pound glass wool
1 pair gloves, asbestos
1 manifold for introduction of sample to chromatograph (may require 3 stopcocks and 2 female ball joints)
1 funnel, filter, for filling columns
1 syringe, gas, 1-ml
1 syringe, liquid, 1-microlitre
1 syringe, liquid, 10-microlitre
1 lecture bottle each of ethane, propane and butane
1 pint each of iso- and normal pentane
1 cylinder of Natural Gas Calibration Standard, with regulator
1 cutter, tube
2 spanners, shifting
1 pliers
1 set screwdrivers

ANALYTICAL METHOD[1]

Gas Extraction

Gases are removed from soil samples by a procedure similar to that described by Horvitz (1954). In brief, dilute hydrochloric acid is added to a weighed soil sample and the evolved gases are extracted under reduced pressure (30-50 mm) and elevated temperature (50-60°C). The gases pass through potassium hydroxide, magnesium perchlorate and Ascarite traps to remove carbon dioxide, water, and any residual carbon dioxide, respectively, before entering a coiled glass trap immersed in liquid nitrogen (-196°C). At this temperature and pressure (less than 10 mm in this part of the apparatus) the fixed gases, hydrogen, oxygen, and nitrogen, together with methane, do not condense and are removed from the apparatus through the vacuum pump. The hydrocarbons heavier than methane (e.g. ethane, propane, butanes, pentanes) are condensed and remain in the coiled glass trap. This trap is warmed to room temperature before the gas mixture is transferred to the gas chromatograph for analysis.

A detailed description of the extraction procedure is given in a following section. If the extraction routine is strictly followed it should be possible to produce replicate hydrocarbon values for any particular sample to within an accuracy of ±10 per cent.

Gas Analysis

Before the introduction of the modern gas chromatographic techniques the extracted gases were analyzed by low-temperature fractionation and combustion methods (Horvitz, 1954). These procedures required a complicated apparatus, they were time-consuming, and only two separate fractions were determined—methane and ethane plus heavier hydrocarbons. Gas chromatography has now almost entirely superseded the older analytical methods.

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[1] Canadian Patent Application 863, 197.

Detailed Extraction Procedure

1. Sample Preparation

1.1 Dry 100-150 grams of clay sample or 400-500 grams of sand sample overnight in a drying oven at 110°C.

1.2 Crush clay samples with a large mortar and pestle to break up the aggregate. Pebbles and rock fragments should be removed and not pulverized in this operation. Sand samples do not require grinding. Retain some dry uncrushed sample in a paper bag for check analyses, etc.

1.3 Sieve crushed samples through a 200 mesh (Tyler) screen until 30-40 grams of -200 mesh material is obtained. Store both +200 and -200 mesh fractions in small paper envelopes, but use only the -200 mesh fraction for analysis. Mechanical sieving devices may be used for this operation.

2. Gas Extraction Procedure

Although the procedure is essentially a unit operation it is possible to utilize one bank of apparatus continuously. At least three 1-litre flasks and two hydrocarbon (HC) traps are required. The instructions given below should be used in conjunction with the diagram illustrating the apparatus (Fig. 2).

2.1 Smear ball joints of HC trap lightly with silicone vacuum grease and attach trap to apparatus.

2.2 Check CO_2- and H_2O-traps (containing saturated KOH solution, granular magnesium perchlorate, and Ascarite) and adjust levels or replace as required. If KOH liquid level is too high, excessive bubbling will cause liquid to pass between traps, resulting in crystallization and line blockage. Tubing jets in liquid traps must be cleared of crystals. Magnesium perchlorate with a damp appearance must be replaced or water will enter the HC trap and freeze, possibly blocking the trap.

2.3 Ensure that all stopcocks except 9 are closed (9 remains open to the line during analyses; it supplies a convenient point to obtain vacuum for filling columns or testing traps, etc.).

	Elapsed time from start in minutes
2.4 Open stopcocks 8, 7, 6 and 5 in that order to evacuate traps (if no adjustments were required the traps between 4 and 5 may already be evacuated from previous extraction).	0

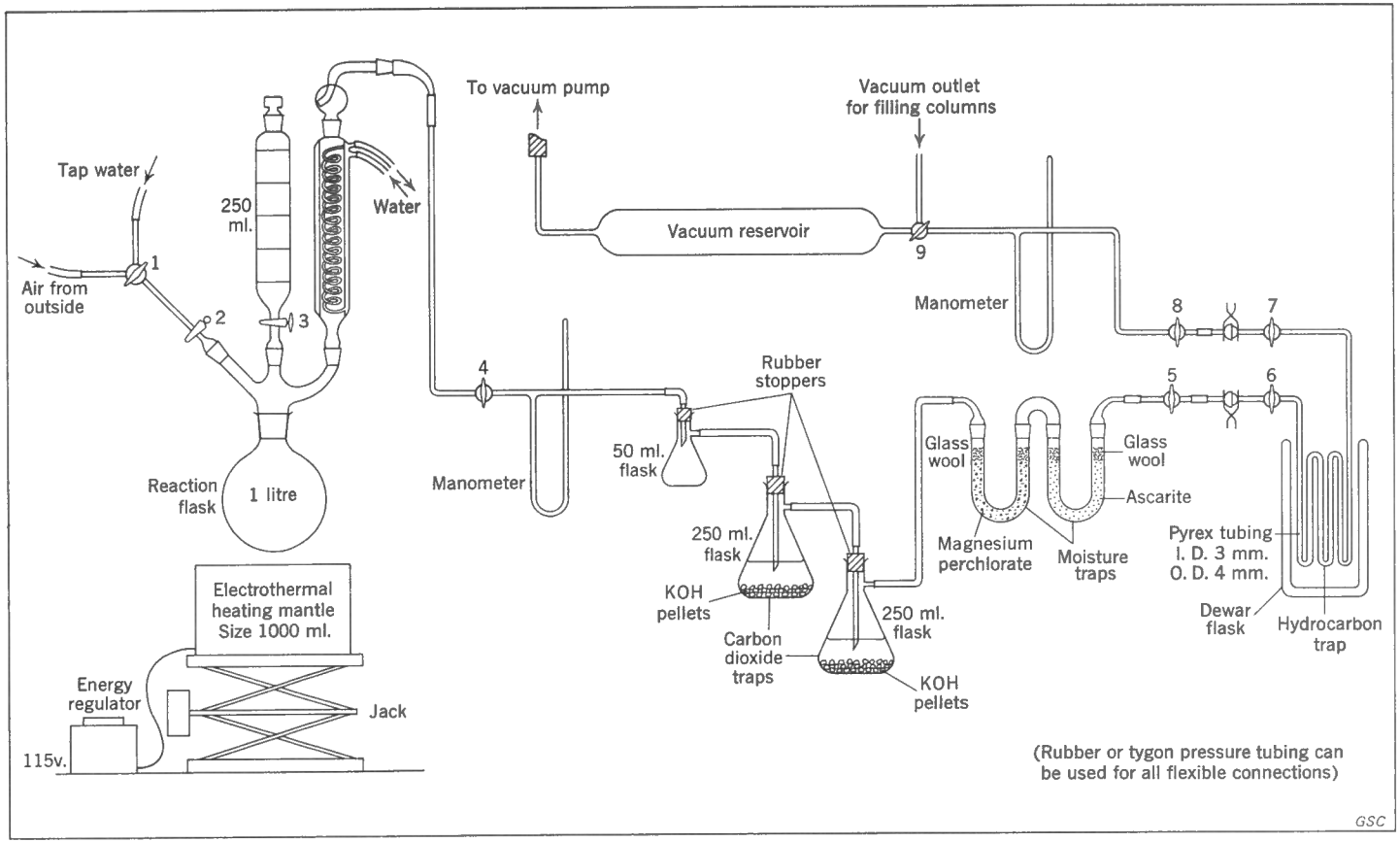

Figure 2. Apparatus for extracting hydrocarbons from soils

		Elapsed time from start in minutes
2.5	Raise Dewar flask to immerse HC trap in liquid nitrogen and top up liquid level to cover trap completely. (The trap will cool for about 4 1/2 minutes before extraction commences.)	
2.6	Remove reaction flask from apparatus and replace with flask containing weighed sample (5, 10, 20 grams etc.). The neck of the flask should be lightly smeared with silicone grease.	
2.7	Ensure that the dropping funnel contains sufficient acid for the analysis and that water is flowing through the condenser.	
2.8	Open stopcock 4 to evacuate flask through the traps. Pressure in the flask will be about 50 mm within 3 minutes.	2
2.9	Slowly add the required amount of acid (100 ml 2N HCl for 10-gram sample) by controlling stopcock 3 to prevent excessive reaction carrying sample above the neck of the flask.	5
2.10	Raise the heating mantle to the flask with regulator adjusted to maximum heat.	
2.11	Continue extraction for 15 minutes. Control refluxing to about half-way up the condenser by periodic adjustments to the regulator. (If cooling water in condenser is not cold, a second condenser may be required to prevent excessive moisture passing into the CO_2 trap.)	
2.12	Reduce heat and lower heating mantle. Turn stopcock 1 to water inlet and open 2. Slowly add water to flask by adjusting flow at tap. Stop water when level reaches neck of flask, close stopcock 2 and turn 1 to air inlet. Allow apparatus to evacuate for 3 minutes to enable air (from water) to sweep any residual gases into the HC trap.	20
2.13	Close stopcocks 4, 5, 6, 7 and 8 in that order. Lower liquid nitrogen flask from HC trap and remove trap from apparatus.	24
2.14	Place new trap on apparatus as described in step 2.1.	

	Elapsed time from start in minutes
2.15 Open stopcock 2 to bring pressure in flask to atmospheric. If at this stage any adjustments are required to the CO_2-water-traps (step 2.2) air must be introduced to these traps from the flask via stopcock 4. Close 4 when traps are at atmospheric pressure.	
2.16 Close stopcock 2 and turn 1 to closed position.	
2.17 Continue with steps 2.3, 2.4, 2.5, 2.6, 2.7 and 2.8 as described above in preparation for the next extraction.	25 (0) or 30 (0) if traps adjusted
2.18 The HC trap removed from the apparatus in step 2.13 should be warmed to room temperature before analysis is commenced. (This takes about 5 minutes, during which time it can either be on the bench or attached to the gas chromatograph.) If HC traps tend to accumulate (i.e. determination is slower than extraction) they may be stored in a liquid-nitrogen bath.	
2.19 While step 2.11 is in progress the operator should perform the steps detailed below as time permits.	
2.19.1 Weigh required amount of the next sample into a 1-litre reaction flask (glass beads can be added if required).	
2.19.2 Prepare 2N HCl when necessary and add acid to dropping funnels as required.	
2.19.3 Continue determination of solubles[1]. The residue in the reaction flask (removed from apparatus in step 2.6) is allowed to settle until liquid is fairly clear (usually about 30 minutes). Decant the upper 500 ml to waste and stir the	

[1] The solubles are determined in order to obtain a factor for converting the gas content of the total soil sample to the gas content of the soluble material in the soil sample. It is possible that by using this information the soil-gas anomalies in the vicinity of oil and gas fields may be more accurately outlined.

Elapsed time from start in minutes

remaining 500 ml before transferring to a 1-litre beaker. Wash flask with several portions of distilled water, adding washings to beaker. If clay particles adhere to the flask they may be dislodged with the aid of a suitable tool (e.g. cotton-wool swab on end of a piece of bent 1/8-inch copper tube). Stand beaker overnight or until sediment settles. Decant the clear liquid and transfer sediment to a 250-ml beaker using wash bottle. Fill the small beaker with hot water, stand until sediment settles (30 minutes), decant liquid and dry residue in an oven at 110°C (several hours or preferably overnight). Remove dry residue from beaker, weigh, and record weight. The difference between weight of original sample and residue is the weight of soluble material in the sample. Any suitable filtering procedure may be used to recover the residue, provided clay material is not lost.

2.20 Analysis of the HC sample in the trap should take 14 minutes, and another 9 minutes are required for cooling the chromatographic column, giving a total time of 23 minutes per sample.

2.21 If total hydrocarbon determinations are not required the 2N HCl can be replaced by 0.05N HCl and step 2.19.3 omitted.

3. Productivity

As time for both extraction and analysis is 25 minutes or less (an occasional 30 minutes for extraction), one operator using one extraction unit and one gas chromatograph should complete 15 samples per 8-hour day. The extraction unit is operated as described above while the column is being cleared and cooled in the gas chromatograph.

Sample preparation is an independent operation. Under favourable conditions a productivity of 25-30 samples per man-day should be possible.

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