Gas Chromatographic and Associated Methods for the Characterization of Oils, Fats, Waxes and Tars. 1982

Methods for the Examination of Waters and Associated Materials

London: Her Majesty's Stationery Office. £6.30 net

Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection' Public Health Laboratory Service Monograph 6, HMSO, London.

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case. all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

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Gas Chromatographic and Associated Methods for the Characterization of Oils, Fats, Waxes and Tars 1982

Methods for the Examination of Waters and Associated Materials

This booklet contains five methods, which together with other methods in this series can be used for the examination of waters and associated materials for oils, fats, waxes and tars. See: About these methods – below.

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London Her Majesty's Stationery Office

About this series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains short reviews of the more important analytical techniques of interest to the water and sewage industries. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users — the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standards Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has seven Working Groups, each responsible for one aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological methods
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in the booklet.

T A DICK
Chairman

L R PITTWELL
Secretary

3 February 1983

About these methods

0.1 It is the long term objective of the Oils Fats and Waxes Panel of the Standing Committe of Analysts to produce a comprehensive scheme of analysis for the characterization of oils, fats, waxes and tars which can cause pollution of fresh and saline waters.

0.2 A series of quantitative and qualitative methods will eventually be co-ordinated into a General Scheme of Characterization of Oil, Fat, Waxes or Tar Pollutants which will be published as a separate document (8).

0.3 The methods included in this publication are concerned with gas chromatographic characterization of oil pollutants and cover:

A Low resolution gas chromatography – General method
B Low resolution gas chromatography of Methyl esters of natural oils and fats.
C The recovery of oil from heavily polluted water samples and the preparation of distillate and residue fractions of the oil.
D High resolution gas chromatography
E Identification of gas oil by the isolation of the chemical markers.

When an oil, fat, wax or tar of unknown character has been isolated from a pollution sample, it may be characterized broadly by low resolution gas chromatography (LRGC). More precise characterization of natural oils and fats may be obtained by transesterification and further LRGC and of oils and tars by high resolution gas chromatography (HRGC), particularly on a prepared distillate. A thin layer chromatographic procedure for the identification of gas oil markers has been included because when diesel fuel oil has been characterized by LRGC or HRGC there is usually a requirement to determine whether it is, or is not, rebated (ie contains marker compounds).
The scheme of use of these methods is summarized in Figure 1.

0.4 Chromatographic methods are very sensitive to minor physical and chemical variations in the quality of the materials and apparatus used. Hence this method mentions the actual materials used for the evaluation tests. This in no way endorses these materials as superior to other similar materials. Equivalent materials are acceptable, though it must be understood that the performance characteristics may be different, and can vary with batch. It is left to the senior supervizing analyst to evalutate and choose from the appropriate brands available.

The assistance of the Institute of Petroleum is gratefully acknowledged, and especially for permission to use Figures 2, 3 and 6. Other acknowledgements are made in the text.

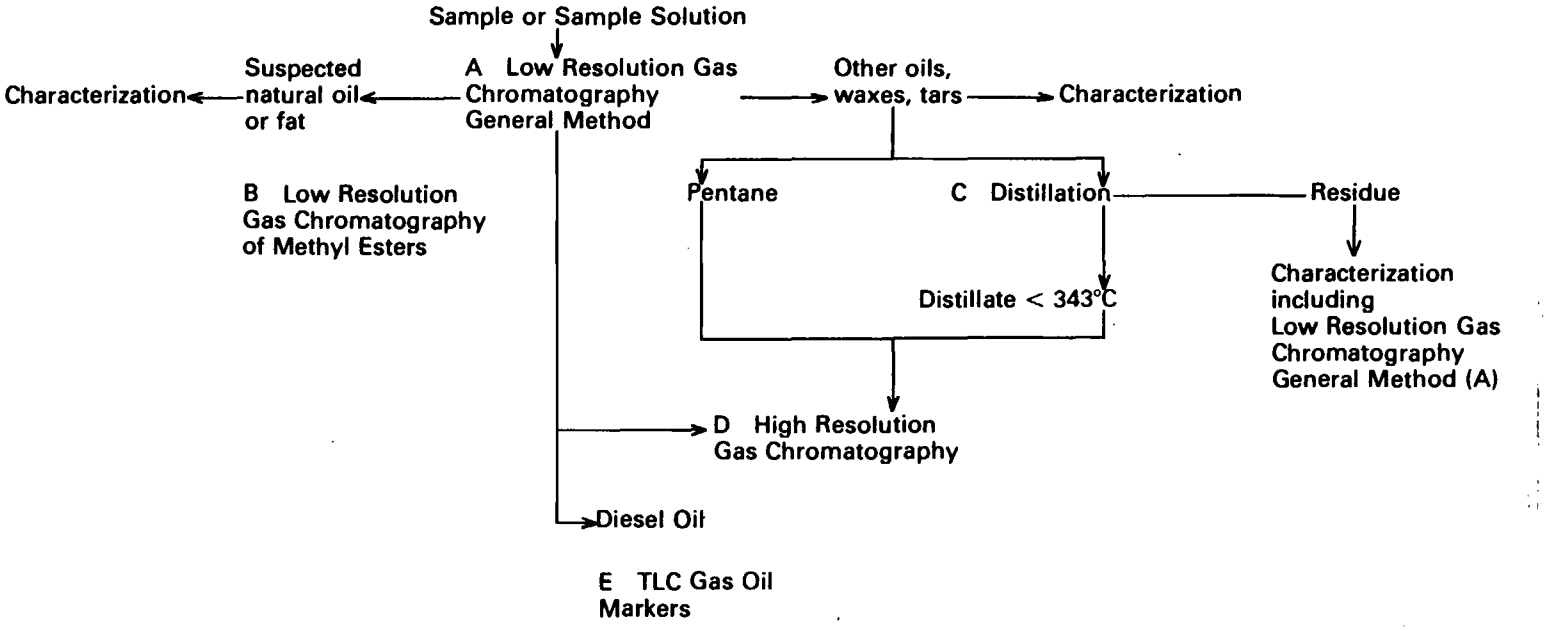


Figure 1 Analytical Scheme for this Booklet

A Low Resolution Gas Chromatography – General Method

A1 Performance Characteristics

A1.1	Substances determined	Oils of petroleum origin. Other oils (eg natural) fats, waxes, tars, bitumens, coal tar and neutral fractions thereof etc. may be classified broadly, but may require further gas chromatographic analysis. Petroleum oils, coal tar and its predominately neutral fraction may be characterized more precisely using high-resolution gas chromatography (see Method D). Oils and fats of natural origin may be characterized more precisely by the preparation of the methyl esters of the fatty acids and their analysis by gas chromatography (see Method B).
A1.2	Types of Sample	Oils, fats, waxes or tars, in liquid, semi-liquid or solid form or the same in solvent solution and residue remaining after distillation (see Method C).
A1.3	Basis of method	Low resolution gas chromatography using flame ionization detection.
A1.4	Interferences	Any compound in a given sample with a GC retention time within the ranges of the oil or tar present in that sample but not a component of the oil or tar.
A1.5	Total time required for analysis (per sample)	From 1 to 2 hr depending on sample type, excluding time for setting up and calibrating gas chromatograph.

A2 Principle

The oil or tar is characterized by programmed temperature gas chromatography. The individual compounds are separated approximately in order of boiling points and displayed on a chart from a recorder as a pattern of peaks, usually superimposed on an 'envelope' of a complex mixture of unresolved compounds, particularly for petroleum oils. The distinctive features of the pattern of peaks are used to characterize the oil. The separation is achieved using dual columns of non polar liquid phases on inert support materials and flame ionization detection. Examples of liquid phases are SE30, 0V1 and 0V101. It is recommended that for inter-laboratory comparison, reference columns should be used as specified by the Institute of Petroleum, viz. 0V1 on Chromosorb G (see Section A6).

A3 Interferences

Any compound in a given sample with a retention time within the range of the oil, fat or tar present in that sample but not a component of the oil, fat or tar will interfere. Oil dispersants can interfere with chromatogram interpretation (reference 1).

A4 Hazards

The aromatic hydrocarbons should be handled with care because long term exposure might induce cancer. The solvents used are flammable and care should be taken to avoid sparks or naked flames during the preparation of standards etc. Use under well ventilated conditions.

A5 Reagents

Analytical or chromatographic grades are to be preferred where available.

A5.1 Hexadecane (C_{16}), octadecane (C_{18}), docosane (C_{22}) and octacosane (C_{28}).

A5.2 Indene, naphthalene, 1- and 2- methylnaphthalene, biphenyl, acenaphthene, dibenzofuran, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene and chrysene.

A5.3 Fatty acids such as lauric acid, palmitic acid, stearic acid and suitable mono, di and triglycerides such as monopalmitin, monostearin, dipalmitin, distearin and trilaurin.

A5.4 It is suggested that typical samples of petroleum oils, tars and tar fractions and natural oils of known character should be kept as reference materials. Wherever possible, samples of oil types from more than one source should be available. The list given below is not comprehensive but represents possible pollutants.

It must be borne in mind that the distribution and types of compounds occurring in samples can vary considerably, resulting in chromatograms of very different appearances. Thus, the use of reference samples is of quite limited value for characterization of samples from individual pollution incidents; the most useful comparisons are those between samples of pollutant and suspected source materials (see section A8). Further information on characterization and the use of reference standards may be found in reference 1.

A5.4.1

Gasoline
Kerosine
White spirit
Diesel fuel oil (35 secs)
Light residual fuel oil (approx. 220 secs)
Medium residual fuel oil (approx. 3500 secs)
Motor lube oil (SEA 20W – 50)
Non-soluble cutting oil
Bitumen (200 pen)
Light crude petroleum oil
Heavy crude petroleum oil
Reference samples of oils (particularly crude oils) may be obtained from Laboratory of the Government Chemist (Oil Identification unit) National Physical Laboratory, Teddington, Middlesex TW11 0LW.

A5.4.2

High temperature tar (coke-oven tar)
Low temperature tar
Creosotes BS144: 1973

Tars are commercially distilled into various fractions with boiling point ranges of 30°C to 100°C. Further details of these fractions can be found elsewhere (reference 2). Creosotes are blends of these fractions conforming to the relevant British Standard. In many cases fractions from the different types of tar (low and high temperature) are blended in various proportions to form creosotes.

If reference samples of coal tar and its products are required an approach should be made in the first instance to the Director and Secretary, British Tar Industry Association, 132/135 Sloane Street, London, SW1X 9BB.

A5.4.3

Coconut oil
Sunflower oil
Rapeseed oil
Palmkernel oil

Natural oils are often modified by chemical processes such as hardening, saponification, etc. and they may appear chromatographically different from the original source material. Animal fats are also found, particularly in sewage samples. Reference samples of natural oils and fats may be obtained from Effluent Section, Unilever Research Laboratories, Port Sunlight, Wirral, Merseyside, L62 4XN.

A5.5 **Solvents** toluene and diethyl ether.

A5.6.1 *Reference Solution A*

Weigh 60 ± 6 mg each of hexadecane, octadecane, docosane, and octacosane into a 100 ml volumetric flask. Make up to mark with toluene.

A5.6.2 *Reference Solution B*

Weigh 60 ± 6 mg each of the compounds listed in Section A5.4.2 into a 100 ml volumetric flask. Make up to mark with diethyl ether.

A6 Apparatus

A6.1 **A dual column gas chromatograph**

fitted with a temperature programmer and flame ionization detectors. If a single column chromatograph only is available this may be used, but will be considerably less effective because of baseline drift particularly at high column temperatures.
A chart recorder is the best form of read out, set at a speed of 1 cm/min.

A6.2 Any suitable sample introduction system may be used. Syringe injection may be used for sufficiently liquid samples or sample contained in appropriate solvents. For analysis of more viscous samples as received, an inlet system is required as specified in the Institute of Petroleum method IP 296/73T which is shown in Figure 2. It consists of two stainless steel ball valves linked together by a stainless steel connector. A vaporization chamber capable of operating at 350°C is attached to a lower valve. A glass tube for holding the sample is illustrated in Figure 3.

A6.3 The columns should have an initial efficiency of about 1500 plates and hence will have a resolution of R greater then 5 where R is measured as follows.

Set the oven temperature at 100°C, inject 1 µl of Reference Solution A and programme the oven temperature to rise at a fixed rate of 5°C/min to 300°C. Defining d as the distance in mm betweeen C_{16} and C_{18} n-alkane peaks at the peak maxima and Y_1 and Y_2 as the widths of the peaks at their bases, ie the distances between the points of intersection, where the tangents to the points of inflection of each peak meet the base time, then the column resolution R may be calculated as follows (see Figure 4).

$$R = \frac{2d}{Y_1 + Y_2}$$

The performance of the column may also be defined using Separation Number n_{sep} (see another Publication (9) in this series) where

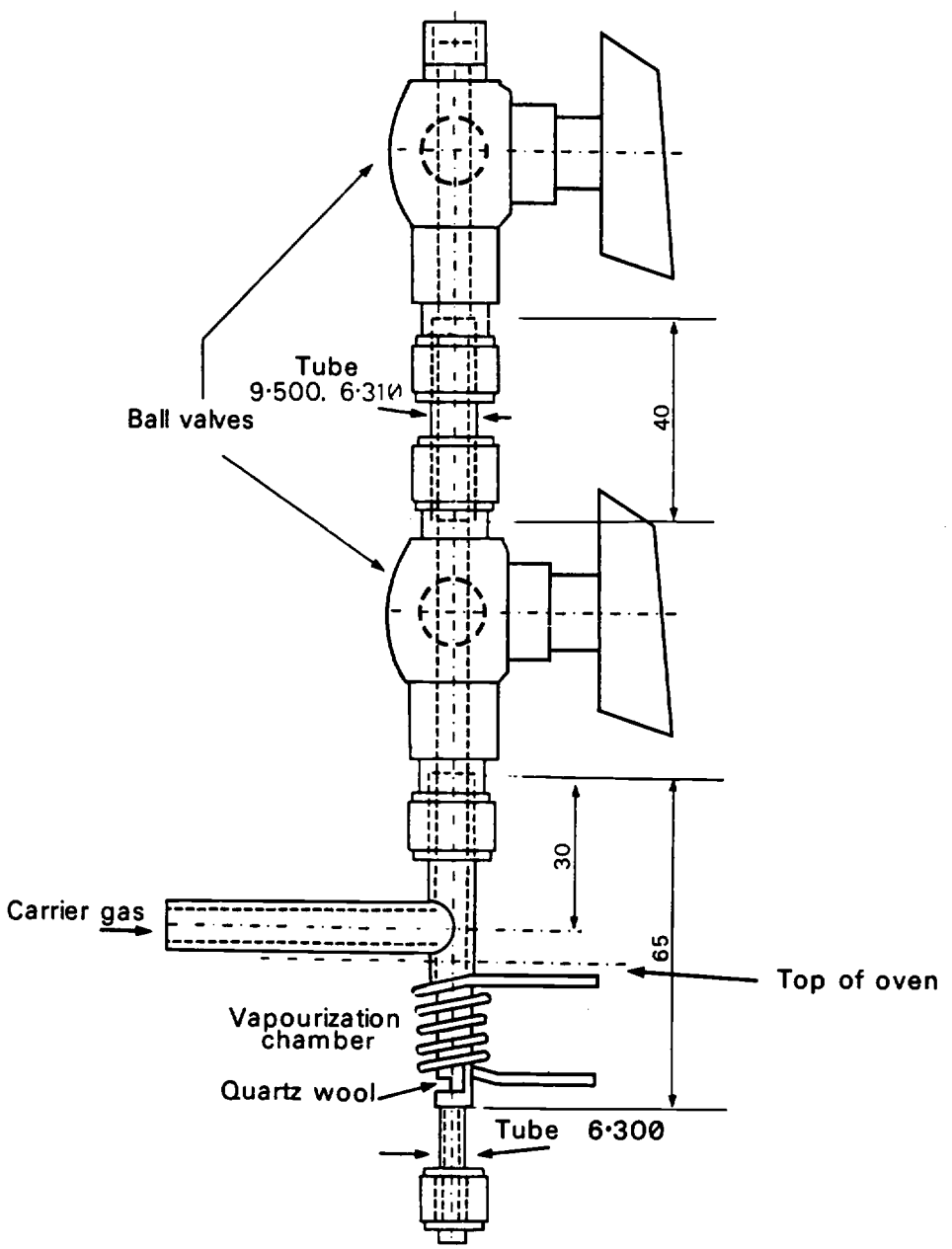
$$n_{sep} = \frac{d}{Y_1 + Y_2} - 1$$

d = distance between C_{16} and C_{17} peaks
Y_1 = peak width at half height for C_{16}
Y_2 = peak width at half height for C_{17}

If this is used, Reference solution A should be prepared using heptadecane in place of octadecane. n_{sep} should initially be about 5.

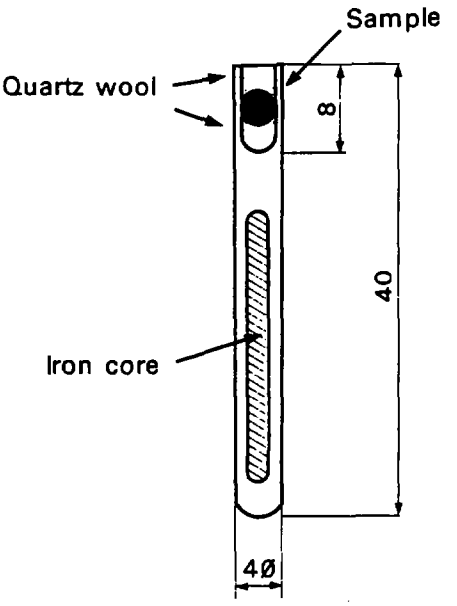
These conditions are achieved by using stainless steel or glass columns of 1 metre length and 3mm internal diameter (although the exact dimensions will vary according to the make of instrument employed) packed with a non polar stationary phase coated onto an inert support. The use of 5% 0V1 on Chromosorb G 80–100 mesh AW–DMCS is recommended for inter-laboratory comparisons as in IP 296/73T.

Figure 2 INLET SYSTEM



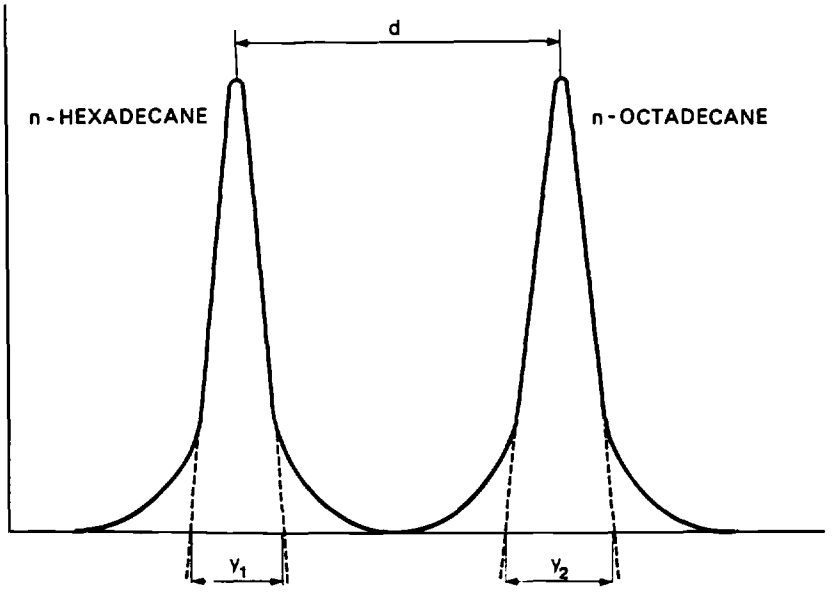
The typical dimensions given are in millimetres, but are not critical as long as the tube (Fig. 3) can pass through the two valves from the top entry to the vapourization chamber which is connected to the chromatograph.

Figure 3 SAMPLE TUBE



Dimensions are in millimetres; but see Fig. 2

Figure 4



A7 Analytical Procedure

Step	Procedure	Notes
	Preparation of instrument	
A7.1	Set up instrument according to the manufacturer's instructions. The injection port heater and detector oven should be set at 300–350°C. The carrier gas should be helium or oxygen-free nitrogen (note a) set at an appropriate flow rate to give the performance specified in Section 5.3. The programmer should be set for a range of 100°C to 300°C at a fixed rate of 5°C/min (see note b).	(a) When oxygen-free nitrogen is used, it may be necessary to pass it through a deoxygenater to prevent column deterioration. (b) 4 to 6°C/min may be used.
A7.2	Equilibrate the column to obtain a steady base-line (see another Publication (9) in this series) (note c).	(c) The columns must have been previously stabilized (see another Publication (9) in this series) by disconnecting them from the detectors and operating the column oven at 300°C for 12 hours with carrier gas flowing. Maintain 300°C and inject 10 × 2μl quantities of Kuwait crude oil
A7.3	Adjust the gas flow rates so that the hydrocarbon retention times on both columns are the same by injecting 1 μl portions of Solution A, and chromatographing under the conditions set out in Steps A7.5–A7.7 (see note d).	(d) Docosane should elute in 17 ± 2 mins and octacosane in 23 ± 2 mins for columns as specified in IP 296/73T (reference 1)
A7.4	The retention time between different programmed temperature runs should be within 45 seconds of each other. These should be checked by injecting 1 μl portions of Solution A as in A7.3.	
	Gas chromatography	
A7.5	Set the oven temperature at 100°C and maintain this temperature for 20 mins.	
A7.6	If the sample is contained in a solvent or is a mobile liquid, then 10 μl or 1 μl respectively should be injected onto the column. If the analysis of a more viscous sample as received is required, weight accurately about 3 mg of solid sample onto a small amount of quartz wool contained in the sample holder. Retain the sample in the tube with a further layer of quartz wool. Allow the tube to fall onto the apparatus, open-end first, through the injection system by opening and closing the two valves successively.	
A7.7	On injection, programme the oven temperature to rise to 300°C at the rate of 5°C/min, and leave the column oven at 300°C until the chart pen returns to within 3% of full-scale deflection of the original base-line (see notes e and f).	(e) If a single column chromatograph is used the base-line will not return to within 3% of the original line due to uncompensated increased column bleed.
A7.8	On completion of the analysis, if a sample tube was used, withdraw it through the ball valve with a magnet. Cool the oven and return to Step A7.5.	(f) The sample size and chromatograph attenuation should be such that the largest peak in the chromatogram has between 60% and 90% of full-scale deflection.
A7.9	Each sample must be run on both columns alternately.	

Step	Procedure	Notes
A7.10	Repeat the procedure using appropriate reference materials. The sample is characterized by comparison to those reference materials and in the case of coal tar and its fractions by comparison with a chromatogram produced by chromatographing Reference Solution B (see note g).	(g) The columns should be checked regularly with Reference Solutions A, B or C, and typical reference materials as the performance deteriorates with use. n_{sep} should not fall below 1 (about 600 plates) and the peaks should not become significantly asymmetric.

A8 Characterization

A8.1 Samples of oil pollutant may be characterized by comparison of features of their gas chromatograms with those of typical known oils. However, because oil and tar types can vary widely in chromatographic nature the ability of the method to provide a precise characterization is often constrained by the number of typical oil samples available. The analyst is advised to compile a comprehensive library of chromatograms and to have access to a wide range of typical oils and tars.

Oils isolated from pollution incidents can be mixtures or modified in nature primarily due to loss of volatile component during weathering (reference 1). One of the most effective ways of using gas chromatograms is by comparison of the pollutant and suspected source irrespective of the exact characteristics of either (see A Comprehensive Scheme for the Identification of Oils, Fats, Waxes and Tars, to be published in this series).

A8.2 Examples of various petroleum oils are given in Appendix 1. The most abundant peaks stand out from the broad envelope, those predominating being due to n-alkanes. The most valuable features are:

A8.2.1 The boiling range of the sample.

A8.2.2 The presence or absence of n-alkanes in the material as a whole (n-alkanes are preferentially biodegraded).

A8.2.3 The presence or absence of n-alkanes above about C_{32}:

A8.2.4 The presence or absence of characteristic components.

A8.2.5 Evidence of fractionation and blending.

A8.3 Examples of various tars and creosotes are given in Appendix 1.
The most valuable features are:

A8.3.1 The boiling range of the sample.

A8.3.2 The complexity of the pattern of components

A8.3.3 The relative amounts of the major components.

A8.4 Examples of various natural oils are given in Appendix 1. The most valuable features are the presence of free fatty acids and/or glycerides which will, for example, indicate the degree of saponification. If it is suspected that the pollutant is an essential oil, then characterization may be obtained, use of 2m columns of 15% carbowax 20 M on Chromosorb WHP AW–DMCS 80–100 mesh or 12% carbowax 20 M Gas-Chrom Q 80–100 mesh temperature programmed 75 to 230°C min^{-1} has been found to be satisfactory (reference 3).

A8.5 Comprehensive assistance in characterization may be found elsewhere in the literature (reference 1), but a few general points are useful viz:

A8.5.1 Oils of petroleum origin with volatile components, eg diesel oil and residual fuel oils, normally give chromatograms showing regularly spaced peaks.

A8.5.2 Oils of petroleum origin with relatively involatile components, eg lubricating oils, normally give chromatograms with a broad envelope and a few individual peaks.

A8.5.3 Coke oven tar and its fractions normally give patterns where the peaks due to unsubstituted aromatic hydrocarbons and heterocyclic compounds (those listed in Section A5.2) predominate.

A8.5.4 Low temperature tar and its fractions normally give more complex patterns with little or no predomination by peaks due to unsubstituted aromatic hydrocarbons.

A8.5.5 Oils of natural original normally give relatively simple chromatograms consisting of a few irregularly spaced peaks.

A8.6 More precise identification of pollutant oils and tars may be obtained by the use of high-resolution gas chromatography. (See Methods C and D) Oils and fats of natural original may be characterized more precisely by the preparation of the methyl esters of the fatty acids and their analysis by gas chromatography (see Method B).

B Low Resolution Gas Chromatography of Methyl Esters of Natural Oils and Fats

B0 Introduction

When a pollutant is classified tentatively as a natural oil or fat by low resolution gas chromatography (Method A) it may be necessary to obtain more precise classification. This can be established by low resolution gas chromatography of the methyl esters of the fatty acids formed by the saponification of the fat or oil.

This method is based on the ISO Methods Nos. ISO 5508 and 5509 - 1978(E) (references 4 and 5).

B1 Performance Characteristics

B1.1	Substance determined	Natural oils and fats.
B1.2	Types of sample	Oils or fats; if in solution, the solvent should be removed.
B1.3	Basis of method	Transesterification followed by low resolution gas chromatography and flame ionization detection.
B1.4	Interferences	Compounds that will form methyl esters (synthetic carboxylic acids) or other compounds that have the same g.c. retention times as the methyl esters derived from the sample.
B1.5	Total time required for analysis (per sample)	Esterification ~ 0.5 hours Chromatography ~ 1.0 hours depending on sample type excluding time for setting up and calibrating gas chromatograph.

B2 Principle

The natural oil or fat is saponified, if necessary, and the fatty acids converted to the methyl esters and then analysed by gas chromatography. The quantitative interpretation of the chromatogram can then be utilized to determine the composition of the sample.

B3 Interferences

Any compound in a given sample with a GC retention time within the range of oil or fat present in the sample, but not a component of the natural oil or fat will interfere.

B4 Hazards

Boron trifluoride is a toxic compound. Preparation of the solution B5.2 on the premises from boron trifluoride and methanol is not recommended. Carry out all manipulations involving boron trifluoride in a fume cupboard. Clean glassware immediately with water. Heptane is flammable and care should be taken to avoid naked flames or sparks during its use. Use under well ventilated conditions.

B5 Reagents

Analytical or chromatographic grades are to be preferred where available.

B5.1 **Methanolic sodium hydroxide** approximately 0.5N. Dissolve 2.0 ± 0.1 g sodium hydroxide in 100 ± 1 ml methanol containing not more than 5% m/m of water. Store the methanolic sodium hydroxide solution in a closed vessel eg a polythene bottle with screw cap. On prolonged storage a precipitate of sodium carbonate may form; this does not influence the methyl ester preparation.

B5.2 **Methanolic boron trifluoride solution** approximately 14% m/m (14% m/m and 50% m/m methanolic solutions are available commercially.)

B5.3 **Heptane** Chromatography grade

B5.4 **Sodium sulphate** Anhydrous

B5.5 **Sodium chloride solution** Saturated, aqueous.

B5.6 **Reference materials**

B5.6.1 It is suggested that typical samples of natural fats and oils of known character be kept. It must be borne in mind that whilst chromatograms for oils of the same type are similar, variations do occur according to the source and history of a given sample. The most useful comparisons are those between samples of pollutant and suspected source materials.
Further information on characterization may be found in reference 6. The list given below contains natural oils used commonly:

Coconut oil
Sunflower oil
Rapeseed oil
Palmkernel oil

Animal fats are also found particularly in sewage samples. Reference samples of natural oils and fats may be obtained from Effluent Section, Unilever Research Laboratories, Port Sunlight, Wirral, Merseyside, L62 4XN.

B5.6.2 It may be necessary to prepare a mixture of synthetic methyl esters for the purpose of identifying individual components in a sample, if this is so, prepare references solutions A and B.

B5.6.3 **Reference Solution A** Weigh 150 ± 5 mg of each methyl ester of the even numbered straight chain acids from C_6 to C_{20} into a 25 ml graduated flask; make up to volume with n-heptane.

B5.6.4 **Reference Solution B** Weigh 150 ± 5 mg of methyl oleate and of methyl stearate into a 5 ml graduated flask; make up to volume with n-neptane.

B6 Apparatus

B6.1 A dual column chromatograph fitted with a temperature programmer and flame ionization detectors. If a single column chromatograph only is available this may be used with considerably less effect because of baseline drift, particularly at high column temperatures. A chart recorder capable of responding to 90% full scale deflection in less than 1.5 secs is the best form of read out set at a speed of 1 cm/min.

B6.2 A glass column of 2 metres length with 3 mm internal diameter packed with polar stationary phase (such as diethylene glycol polysuccinate, butanediol polysuccinate, ethylene glycol polyadipate) on an inert support such as Chromosorb W 100 – 120 ethylene glycol polyadipate on Chromosorb W 100 – 200 mesh AW–DMCS. The efficiency and resolving power of the column may be determined by carrying out an analysis of a Solution B (as per Analytical Procedure). Choose the size of the sample, the temperature of the column and the carrier gas flow so that the maximum of the methyl stearate peak is recorded about 15 minutes after the solvent peak and occupies about ¾ of the full scale.

Calculate the number of theoretical plates n (efficiency) by the formula:

$$n = 16 \left(\frac{R_1}{Y_1} \right)^2$$

and the resolution R by the formula:

$$R = \frac{2d}{Y_1 + Y_2}$$

where: R_1 is the retention distance, measured in mm, from the start to the maximum of the peak for methyl stearate, Y_1 and Y_2 are the widths, in mm, of the peaks for methyl stearate and methyl oleate, measured between the points of intersection of the tangents at the inflexion points of the curve with the base line (see Fig. 4),

d is the distance between the respective peak maxima for methyl stearate and methyl oleate;

Operating conditions to be selected are those which will afford at least 2000 theoretical plates for methyl oleate and a resolution of at least 1.25. Additionally, linolenic acid ($C_{18:3}$) should be separable from arachidic acid ($C_{20:0}$) and gadoleic acid ($C_{20:1}$).

B6.3 **Standard laboratory glassware**, including a 50 ml round bottom flask with a ground glass socket and a capillary pipette.

B6.4 10 µl chromatographic syringe.

B7 Analytical Procedures THE FOLLOWING PROCEDURE MUST BE CARRIED OUT IN A FUME CUPBOARD BECAUSE OF THE TOXIC PROPERTIES OF BORON TRIFLUORIDE.

Step	Procedure	Notes
	Saponification of Samples Containing Fats and Oils (see Note a)	
B7.1	Heat the dry sample to just above its melting point if the fat is not entirely liquid.	(a) If the sample consists of fatty acids only, saponification is not necessary and 2 ± 0.5 ml of the boron trifluoride solution is added directly to 150 ± 0.5 mg of the sample in the round bottom flask. The mixture is then boiled for 2 to 3 mins under total reflux, 5 ± 0.5 ml heptane added via the condenser and boiled for another minute. The preparation then follows the procedure described under 'Conversion to methyl ester', continuing from stage B7.5.
B7.2	Transfer 150 ± 10 mg of this sample to the 50 ml round bottom flask with a Pasteur capillary pipette. Add 4 ± 0.1 ml methanolic sodium hydroxide solution and a few boiling chips.	
B7.3	Connect the flask to the reflux condenser and boil the mixture under total reflux until all fat globules have dissolved, ie until saponification is complete. Minimum boiling time is 5 minutes.	
	Conversion to Methyl Ester	
B7.4	Add 5.0 ± 0.05 ml of boron trifluoride solution to the boiling mixture via the condenser, using the graduated pipette with the pipette filler. Boil the mixture for 2 to 3 minutes, add 5.0 ± 0.5 ml heptane to the boiling mixture via the condenser and boil for another minute.	

Step	Procedure	Notes
B7.5	Remove the flask from the heat source, cool, remove the reflux condenser, add some saturated sodium chloride solution (usually about 20 mls) and swirl the flask gently several times. Add more of the saturated sodium chloride solution to bring the liquid level of the mixture into the neck of the flask.	
B7.6	Transfer, using a Pasteur pipettte, about 1 ml of the upper (heptane) layer into a glass-stoppered test tube. Add anhydrous sodium sulphate to the test tube to bind traces of water. The solution of fatty acid methyl esters is now suitable for injection on to a gas chromatographic column.	
B7.7	If it is necessary to keep the transesterified sample overnight, store it under an inert gas in a flame-proof refrigerator.	
	Gas Chromatography **Preparation of instrument**	
B7.8	Set up the instrument according to manufacturers instruction including detector optimization. The injection port heater and detector oven should be set at 200°C. The carrier gas should be helium (note b) at a flow to give suitable resolution (note c).	(b) Oxygen free nitrogen may be used but it must be passed through a deoxygenator. (c) As a rule, 20–40 ml/min figures will lead to the desired results, viz. at least 2000 theoretical plates for methyl stearate and its elution within about 15 mins: see Section B6.
B7.9	The initial and final temperature and programme rates should be set according to the nature of the sample (notes d and e) deduced from Method A and other classical techniques (Methods to be published subsequently). The programmer should be set for a rate of increase of 5°C/min (4 to 6°C/min may be used).	(d) The usual initial temperature is 125 °C, but if the acids are below C_{12} it is 100°C and if butyric acid is present, 60°C. (e) Conc. of stationary phase %: 5, 10, 15, 20 Optimum final temp °C: 175, 180, 185, 185
B7.10	Equilibrate the columns at minimum oven temperature required to obtain a stable baseline (see another Publication (8) in this series and note f).	(f) The columns must have been previously stabilized (see another Publication (9) in this series) by disconnecting them from the detectors and operating the column oven at 185°C with the carrier gas at a rate of 20–60 ml/min for at least 16 hours and at 195°C for 2 hours.
	Chromatography	
B7.11	Inject 1 μl of the heptane solution and allow the esters to elute; leave the column oven at 185°C until the chart pen returns to within 3% of full scale deflection of the original base line (see notes g and h).	(g) If a single column chromatograph is used the base line will not return to within 3% of the original line due to uncompensated increased column bleed.

Step	Procedure	Notes
		(h) The sample size and chromatograph attenuation should be such that the largest peak in the chromatogram lies between 60% and 90% of full scale deflection. The volume injected can range between 0.1 and 20 µl according to the proportions of esters present in the original oil.
B7.12	Each sample must be run on both columns alternately (see note i).	(i) It is important that the chromatographic peaks are resolved sufficiently to permit further examination. In some exceptional cases, it has been found necessary to use a variety of non-polar stationary phases to achieve characterisation (See reference 4).

B8 Characterization

B8.1 Qualitative

B8.1.1 Samples of oil pollutant may be characterized by comparison of features of their gas chromatograms with those of typical known oils or with those of suspected source materials. The characterization of such materials is best effected when supported by other chemical and physical tests. (See another Publication (8) in this Series).

B8.1.2 The saturated methyl esters in solution A elute sequentially; construct a graph of the logarithm of retention distance (or time) as a function of the number of carbon atoms. This will not be linear because of the effect of temperature programming (see Figure 5). Sample chromatogram peaks can be identified from these graphs if necessary by interpolation. Unsaturated ester peaks do not fit this curve. Typical chromatograms for the reference oils and fats are given in (Appendix II).

B8.2 Quantitative

B8.2.1 The character of a natural fat or oil is determined by the relative proportions of different glycerides which are present; the measurement of these proportions in a given sample is, therefore, an aid to its characterization. Table 1 and reference 6 give typical compositions of relevant natural fats and oils.

B8.2.2 In such cases, apart from certain exceptions, the method of internal normalization is used, ie assume that the whole of the components of the sample are represented on the chromatogram, so that the total of the areas under the peaks represents 100 per cent of the constituents (total elution).

If the equipment includes an integrator, use the figures obtained therefrom. If not, determine the area under each peak by triangulation (multiply the height by the breadth at mid-height) and, where necessary, take into account the various attenuations used during the recording.

B8.2.3 *The general case*

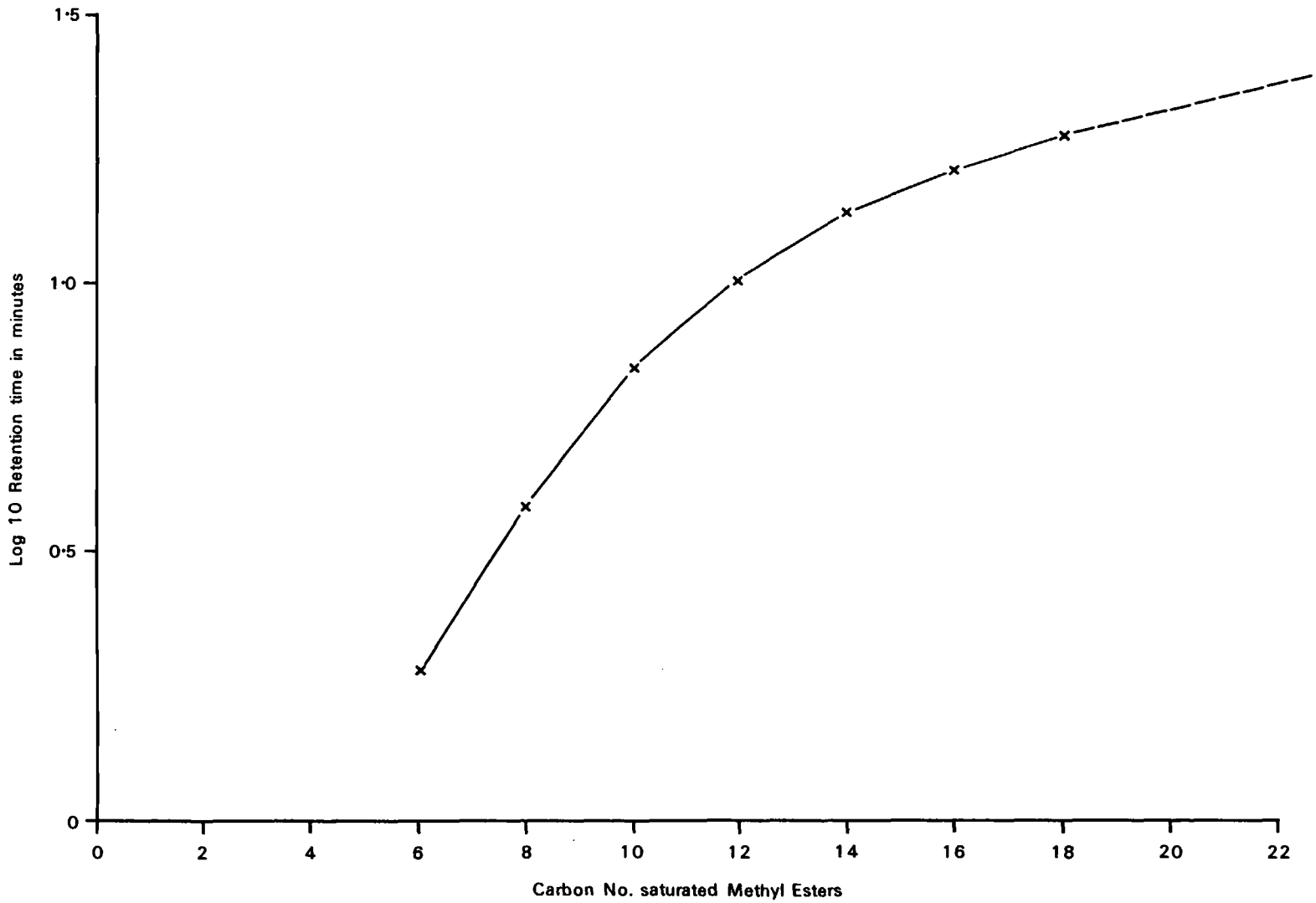
If significant amounts of components below C_8 are absent, calculate the content of a given constituent (expressed as per cent of methyl esters) by determining the percentage represented by the area of the corresponding peak relative to the sum of the areas of all the peaks.

Per cent m/m of the component i expressed as methyl ester:

$$= \frac{A_i}{\Sigma A_i} \times 100$$

A_i = area of the peak corresponding to component i,
ΣA_i = sum of the areas under all the peaks.

Figure 5


1·5
1·0
0·5
0
Log 10 Retention time in minutes
0
2
4
6
8
10
12
14
16
18
20
22
Carbon No. saturated Methyl Esters

B8.2.4 *Use of correction factors*

In certain cases, particularly in the presence of acids below C_8 or of acids with secondary groups, correction factors must be used to convert results calculated as per cent of peak areas into per cent mass of the components.

Determine the correction factors with the help of a chromatogram derived from the analysis of a reference mixture of methyl esters of known composition under operating conditions identical with those used for the sample.

For the reference mixture:

$$\text{per cent m/m of component i} = \frac{B_i}{\Sigma B_i} \times 100$$

B_i = mass of component i in the reference mixture,
ΣB_i = total of the masses of the various components of the reference mixture.

From the chromatogram of the reference mixture the following can be calculated:

$$\text{per cent area/area of component i} = \frac{C_i}{\Sigma C_i} \times 100$$

C_i = area under the peak corresponding to component i,
ΣC_i = sum of the area under all the peaks.

Whence:

$$\text{correction factor } K_i = \frac{B_i \times \Sigma C_i}{C_i \times \Sigma B_i}$$

Commonly, the correction factors are made relative to $K_{16}=1$, so the relative factors become:

$$K_i = \frac{K_i}{K_{16}}$$

Then for the sample, the content of each component is given by: per cent m/m of component i, expressed as methyl ester:

$$= \frac{Ki \times Ai}{\Sigma (K_i \times A_i)} \times 100$$

B8.2.5 *Use of an internal standard*

In certain cases (notably the assay of C_4 and C_6 acids and the examination of the acids when all the fatty acids are not eluted) an internal standard should be used (C_5 and C_{15} or C_{17} respectively) and the correction factor for the internal standard should be determined.

per cent m/m of component i, expressed as methyl ester:

$$= \frac{m_s \times Ki \times A_i}{m \times Ks \times A_s} \times 100$$

m_s = mass, in mg, of the internal standard,
m = mass, in mg, of the sample,
K_s = correction factor for the internal standard,
A_s = area of the peak corresponding to the internal standard,
A_i = area of the peak corresponding to component i.

B8.2.6 *Expression of the results:*

Give the results to 3 significant figures for contents over 10 per cent
to 2 significant figures for contents between 1 and 10 per cent.
to 1 significant figure for contents below 1 per cent.
ie with one figure beyond the decimal point in every case.
Contents less then 0.1 per cent should be expressed as <0.1%.

B8.2.7 The method normally reproduces peak area to within limits of ±5% area (rsd) which is quite sufficient for these purposes.
This reproducibility decreases for a component when it comprises less then 5% of the whole.

B8.2.8 In attempting to characterize an oil or fat sample in the absence of a sample of suspected source material, information given in Table 1 and reference 6 may be used as stated in B5.6.1 and B8.2.1. Particular care must be exercised to ensure that mixtures of oils and single oils are not confused. Where it is suspected that the sample is a mixture and a good indication is obtained for one component, the proportions of the acid for the remaining components may be obtained by correcting the total values with those for the known component. More detailed notes are given in B8.2.9.

B8.2.9 *Notes for the Interpretation of Table 1*

18:1 OH Presence is specific for castor oil (although unstable – still useful)

4:0, 6:0 Presence is specific for milk fat

12:0 More than 1% is characteristic for coconut or palm kernel oil

14:0, 16:1 More than 5% is characteristic for whale oil or fish oil, 2 – 5% may also indicate tallow or lard

22:0 Usually specific for rapeseed oil, provided corrections have been made for whale oil and fish oil, but could be hardened herring oil

18:3 More than 10% is specific for linseed oil, 2 – 10% may indicate soyabean oil. Also rapeseed oil should be taken into consideration because this may have a low erucic acid (13 – docosenoic acid) content and be underestimated.

22:0, 24:0 Indicates arachic oil, provided adequate corrections have been made for rapeseed oil; 22:0 may indicate hardened whale oil or fish oil. More than 1% 24:0 is specific for arachic oil.

16:0 More than 30% is specific for palm oil, 10 – 30% may indicate cocoa butter or cotton-seed oil. Good corrections for other vegetable oil and fats, if present, are essential.

18:2 More than 65% is characteristic for safflower or poppyseed oil. 55 – 60% may also indicate sunflower seed oil and 10 – 15%, cottonseed, sesame, or maize oils. In correcting for arachic oil, allowance for the variable linoleic content should be taken into account and poor corrections may be obtained. In the presence of hardened oil the content of 18:2 gives little information.

It will be noted that for the latter oils the number of alternatives and uncertainties increases. Attempts can be made to decrease this number by using other indications. A distinction can often be made between tallow and lard, by examining odd numbered and branched chain fatty acids and between all lard on the one hand and (hardened) whale oil/fish oil on the other, by examining the 20–22– groups. It will also often be advisable, after an indication is obtained, to go back and recheck early assumptions.

There will also be uncertainty in the characterization and often it will be in the form of a number of alternatives which might be resolved by other tests. The examples given in Table 1 do not include fractionation products. Although fractionation does not generally cause major changes in the fatty acid composition, the deviations may be such that they may lead to false conclusions.

Table 1 Average Fatty Acid Composition Etc of Various Oils and Fats

Type of oil or fat	Hard m.p.°C	Calc. I.v.	Fatty Acid Structure ** 12 :0 %	14 :0 %	16 :0 %	16 :1 %	18 :0 %	18 :1 %	18 :2 %	18 :3 %	20 :0 %	20 :1 %	20 :2 %	20 :n %	22 :0 %	22 :1 %	22 :2 %	22 :n %	24 :0 %	Other fatty acids which may occur Code	%	Code	%	Code	%	Code	%	Code	%
COCONUT		0	47	18	9		2½	7	2½											8:0	8	10:0	6						
.	32	0	47	18	9		12													6:0	8	10:0	6						
PALM KERNEL		16	47	16	8		2½	14	2½											8:0	6	10:0	4						
.	32	10	47	16	8		7	12												8:0	6	10:0	4						
.	30	0	47	16	8		19													8:0	6	10:0	4						
PALM (Sum. type)		52		1	45	½	4½	38	10	½	½																		
.	45	42		1	45	½	9	40	4		½																		
.	53	22		1	45½		30	21	2		½																		
PALM (Nig. type)		57		1	40	½	5	40½	12	½	½																		
.	45	45		1	40	½	11	42	5		½																		
.	53	22		1	40½		34	22	2		½																		
COCOA BUTTER		38			26	½	33	35	4		1				½														
OLIVE		85			11½	1½	2	74	9	1½	½																		
ARACHIC (Nig.		83			10		3½	59	20	½	1½			2½				1½											
. type)	33	70			10		11	54	8		2	1			2½				1½										
. .	45	50			10		30	49	4		2½	½			2½			1½											
ARACHIC (Arg.		102			11		3	39	38	½	1½			3½				2											
. type)	33	79			11		7	61	12½		2	1			3½				2										
. .	45	50			11		28	48	4½		2½	½			3½				2										
COTTON		107		1	23	½	2½	18	52	½		½																	
.	35	72		1	25	½	6	51	16		½																		
.	42	59		1	25	½	13	52	8		½																		
SESAME		113			8½		4½	42	44½		½																		
MAIZE		122			10½	½	2½	32½	62	1	½		½																
SAFFLOWER		147			6		2½	12	78	½		½		½															
.	34	83			6		10	70	13		½		½																
POPPYSEED		144			10		2	11	76	1																			
SUNFLOWER		132			6½	½	5	23	63	½		½		½		½													
.	34	77			6½	½		12½	70	9		½		1															
SOYBEAN		137			10	½		3½	21	56	8	½		½															
.	33	90			10	½		10	53½	25		½		½															
.	45	60			10½		23½	60	5		1																		
LINSEED		192			6½		3½		18	14	59																		
RAPE (Europe		102		½		3½		1	13	14	9	1	7½	1		½		47½	1			½						
SEED type	30	77		½		3½		2	28	7		1	8½			1½	47½		½									
.	45	51		½		3½		13	21	3		4	3½			17	32			½									
RAPE (Canad.		108		½		3½		2	20	17	10	1	12	1		½		31	1			½						
SEED type)	30	82		½		3½		3	35	11		1	13			1½	31			½									
.	45	94		½		3½		17	27	5		6	8			10	22½			½									
RICINUS		91			14		1	4½	6	1		½								OH		16:1	2½	16:1	83			
TALLOW (Bovine)		47		3	26	3½	19½	40	4½											14:1	½	15:0	½	17:0	1	17:1	½	13v	½	17v	1
TALLOW (sheep)		43	½		2	21	3	28	37	4		½		½						14:1	½	15:0	½	17:0	1	19v	½	17v	1	
LARD		62		2	24	4	14	43	9	1	½		1	1								14:1	½						
WHALE		113		9	13	9	2½	25	2½	½			10	1	9		3		10			14:1	1	10:2	1	18:4	1	15:0	½	15:1	½
.																				17:0	½	17:1	½	15v	½				
.	35	79		9	13	10	3	25	2½	1	2	10	6	2	2	4	5	2		14:1	1	17:0	½	15:0	½	19:1	½	15v	½	17:1	½
.	45	42		9	10	5	15	15	1½		6	10	4		3	8				14	1	17:0	½	15:0	½	15:1	½	15v	½	17:1	½
HERRING		121		7	13½	7	1½	15½	2½	1		14½	½			6		19	½		6			14:1	½	16:2	1	18:4	3½	
.	35	73		7	13½	8	0	15	2	1	2	12	4½	3	1	20	3½	1		14:1	½								
.	45	45		7½	19	3½	13	10	1		6	12	2½	1	7	16	2½													
FISH (various)		166		7	18	10½	3	13	2	1		1½	2	16½		1	1½	12½		14:1	½	16:2	2½	16:3	2	10:4	2	15:0	½	15:1	½
																				17:0	1	19:0	½	21:0	1						
.	37	75		7	22	9	7	11	2	1	2	7	8	3	1	4	6	4		14:1	½	15:2	2	15:0	½	15:1	½	17:0	1	19:0	½
																				21:0	1										
.	45	42		7½	26	7	12	8	1		6	8	5	1	5	5	4	1		15:0	½	15:1	½	17:0	1	19:0	½	21:0	1		
MILK		35	3	10	24	3½	13	28½	3		1									4:0	2½	6:0	1½	8:0	1	10:0	2½	14:1	1½		
																				15v	1	15:0	1	16v	½	17v	1	17:0	1		
																				18v	½										

* Iodine Value (see reference 10).
v – branched fatty acids, iso and anti-iso.
OH contains a hydroxyl group

** The fatty acid structure is denoted by a:b where a is the number of carbon atoms and b is the number of double bonds

† The fatty acid contents mentioned above are averages of many determinations in regular trade products. Normal ranges can be indicated roughly as:

Value in table %	Range %
0 – 5	± 1
5 – 10	± 1½
10 – 17	± 2
17 – 25	± 2½
> 25	± 10%

Taking into account experimental errors, larger differences will generally indicate admixtures or the use of raw materials that deviate strongly in composition from usual trade products.

C The Recovery of Oil from Heavily Polluted Water Samples and The Preparation of Distillate and Residue Fractions of the Oil

C0 Introduction

When a pollutant (oil, wax or tar) has been classified by low resolution gas chromatography (Method A), more precise classification may be obtained using high resolution gas chromatography (Method D), and The Comprehensive Scheme for the Identification of Oils, Fats, Waxes and Tars, to be published in this series.

If the results indicate that the sample contains high boiling fractions (ie >343°C) the low boiling fraction may be separated for analysis, by distillation.

The distillation procedure is based on that recommended by the Institute of Petroleum (reference 1). Since the IP method also includes a description of the isolation of oil pollutants from water, the procedure given in this instance has been made comparable, although in may cases the sample to be examined will have been isolated by other techniques and the initial stages of the procedure, ie toleune extraction etc., will not be used.

C1 Performance Characteristics

C1.1	Substances determined	Water, extraneous matter, oil and distillate and residue fractions of the oil.
C1.2	Type of sample	Water samples grossly polluted by oil and particularly those oils containing residual material eg originating from fuel oil, crude oil or discarded tanker washings.
C1.3	Basis of Method	Water is removed from the sample be extractive distillation with toluene. After decantation and filtration of the toluene solution in order to remove insoluble detritus, the oil is recovered from the solution by distillation. The oil can then be fractionally distilled, initially at atmospheric pressure and subsequently at reduced pressure, in order to recover distillate and residue fractions boiling above and below a cut point of 343°C (650°F).
C1.4	Range of application (sample size)	Normal sample sizes will be in the range of 50 ml to a few litres. However the use of small scale apparatus is referenced for sample sizes down to 1 ml.
C1.5	Interferences	Any substances of similar solubility and distillation characteristics to the oil.
C1.6	Time required from the procedure	This will vary considerably depending on the sample size but a typical operator time would be about 1.5 hours with a total elapsed time of about 6.5 hours.

C2 Principle

After any free water has been drained from the pollutant sample. it is diluted with toluene and refluxed in a Dean and Stark apparatus to remove the remaining water; any solid matter is filtered off from the dry solution. The oil fraction is recovered by distilling off the toluene using a fractionating column or stripping apparatus. The distillation can be continued using the fractionating column to prepare a residue boiling above 343°C (650°F) and a distillate fraction boiling below 343°C.

C3 Interferences

Any substances of similar solubility and distillation characteristics to the oil.

C4 Hazards

Toluene is flammable and care should be taken to avoid naked flames or sparks during its use. Use both solvents under well ventilated conditions.

C5 Reagents

Analytical grades are preferred where available

C5.1 **Toluene**

C5.2 **Dichloromethane, redistilled**

C6 Apparatus

C6.1 It is not possible to be specific about the size of apparatus because this will be dependent on the amount of pollutant sample received and experience has shown that this can vary between wide extremes.

For small samples of down to 1 ml the apparatus described in Analytical Chemistry 1955, **27**, pages 991 to 995, is recommended (reference 1).

C6.2 **Round bottomed flask fitted with ground glass socket.**

C6.3 **Dean and Stark graduated (10ml) receiver and a condenser** (see Method ASTM D95/IP74 in Institute of Petroleum Standards for Petroleum and its Products, Part I) Reference 1)

C6.4 **Electric heating mantle.**

C6.5 **Whatman No. 1 filter paper.**

C6.6 **Fractionating column or stripping apparatus**

C6.6.1 A suitable fractionating column assembly is illustrated in Fig. 6; this unit can be used for the recovery of oil samples of approximately 50ml or over. To allow fractions to be taken while the column is operating under reduced pressure, a control system is required which will enable the lower receiver to be vented and re-evacuated without disturbing the operating pressure. This is measured and regulated to the limits given in ASTM method D 2892 in the 1976 Annual Book of ASTM Standards, Part 24. (reference 1)

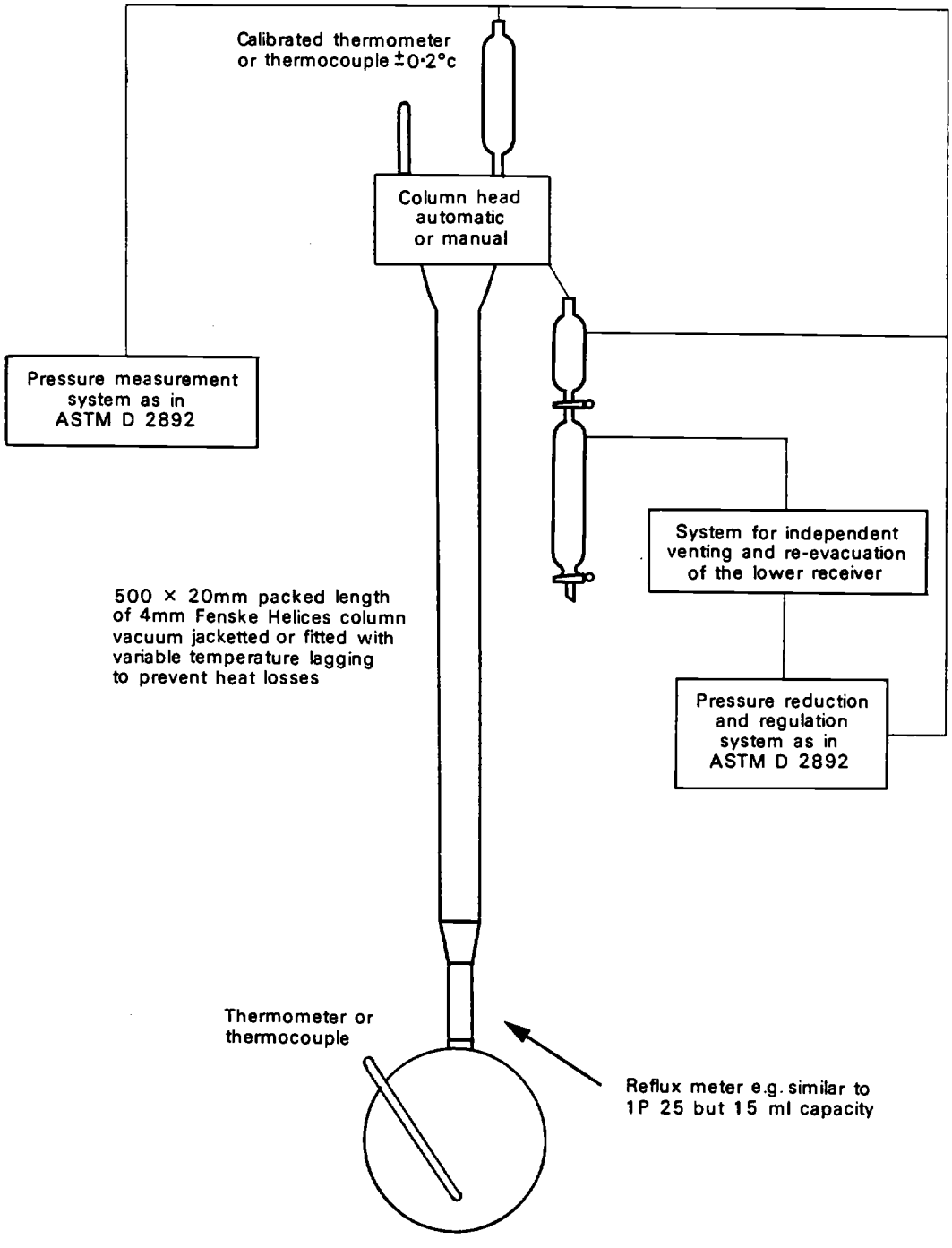
C6.6.2 The solvent stripping can either be carried out using the fractionating column or in a commercial stripping unit or any other appropriate distillation apparatus.

C6.7 Laboratory balance with a precison of at least ±0.1g.

C7 Analytical Procedure

As stated in the Introduction (C.O) this procedure is based on one recommended by the Institute of Petroleum and includes isolation and distillation of the oil pollutant. In most instances the oil will have been isolated by other methods and this procedure should be started at step C7.10, or C7.9 if the oil is in toluene solution.

Figure 6 DISTILLATION UNIT



Step	Procedure	Notes
C7.1	Discard any free water from the sample	
	Removal of water	
C7.2	Transfer of known weight (W_1g) of pollutant to a round bottomed flask with a ground-glass socket at the neck. Use successive portions of toluene for any rinsing that is necessary. Add further toluene to the flask to give a solvent to sample ratio of at least 1 to 2. (notes a and b)	(a) The size of flask is adjusted to the size of sample to be used. The flask should be a half to two-thirds full when sample and solvent have been added. (b) The ratio of solvent to sample is adjusted according to the viscosity of the sample. For the most viscous and semi-solid or solid samples a ratio of solvent to sample of up to 1 to 1 may be used.
C7.3	Using a condenser and a 10 ml receiver with stopcock as described in ASTM D95/IP 74, assemble a Dean and Stark apparatus. (reference 1) Heat the flask using an electric heating mantle. Regulate the heat to give as fast a reflux distillation as possible consistent with not causing flooding at the lower end of the condenser (note c). Remove the water as necessary from the receiver and collect in a bottle. Continue heating until the volume of water in the receiver remains constant for five minutes. Stop heating the flask and allow to cool.	(c) Avoid 'bumping' but if it does occur, place an inverted U-tube on top of the condenser to direct contents into a waste receiver.
C7.4	With a fine wire dislodge droplets of water adhering to the condenser or receiver.	
C7.5	Record the total volume of water removed (V_1ml)	
	Removal of solids	
C7.6	Remove the round bottomed flask from the Dean and Stark apparatus. Decant the dry solution, while still hot, from the solid and filter through a Whatman No.1 filter paper. Collect the filtrate in a tared round bottomed distillation flask (W_2g). Rinse the solids remaining in the Dean & Stark flask with hot toluene until they are clean. Use the hot rinsings to wash any solids in the filter paper. (notes d, e and f).	(d) The filtration and decantation operations involving hot toluene must be carried out in a fume chamber. All sources of ignition must be absent, including outside the exhaust vent; electrical equipment must be spark-proof. (e) If the polluting oil is a waxy sludge, then it will be necessary to keep the filter funnel warm during the filtration. (f) If the pollutant contains large amounts of finely divided solids, these can choke the filter paper making it necessary to use new papers periodically.
C7.7	Collect the solids from the flask and filter paper, using a small amount of toluene, if necessary, to complete the transfer to a weighed evaporating dish (W_3g). Evaporate off the remaining solvent and dry in an oven for 30 mins. at 115°C before weighing (W_4g).	
	Removal of solvent from filtrate	
C7.8	Solvent is removed from the filtrate in an all-glass apparatus preferably with an atmospheric/ vacuum batch fractionating column of about 10 theoretical plates. (note g)	(g) If no fractionating column is available, remove the solvent using a rotary evaporator or an appropriate distillation apparatus.

Step	Procedure	Notes
C7.9	Start the distillation at atmospheric pressure using a boil-up rate of 80 percent of the flood-point and a 2:1 reflux ratio. When the toluene has nearly all been removed, the base temperature will increase and reflux will cease. Cool back to ambient temperature and reduce the operating pressure to 100 ml Hg absolute. Restart the distillation and offtake at 5:1 reflux ratio. The complete removal of toluene is signified either by a rapid increase in observed vapour temperature or a second cessation of reflux. Stop the distillation and, after cooling and venting, remove the distillation flask. Weigh the flask (W_5g) (note h and i)	(h) Any derivation of vapour temperature at pressures other than the operating one is done in accordance with ASTM D 2892, Appendix X.3 (see section C6.6.1 for publication details) (i) Whichever method of toluene removal is used it may be desirable to collect the final portion of solvent. The final portion can then be checked for any loss of lower boiling constituents from the recovered oil.
	Preparation of distillate	
C7.10	At this stage the distillation can either be considered complete and the recovered oil taken from the distillation flask or, after replacing the distillation flask containing the oil, distillation can be continued at a higher reflux ratio (10:1) and subsequent pressure reduction until a corrected cut point of 343°C (650°F) is achieved. If the distillation is continued to the 343°C cut point, the distillate is collected in a tared receiver (W_6g). The distillation is then completed and the unit allowed to cool after careful venting. (note j).	(j) The base temperature must not be allowed to go above 280°C otherwise decomposition of the oil will occur.
C7.11	The column hold-up is recovered by washing down the distillation column packing with dichloromethane into a clean dry flask. After evaporation of this solvent on a steam bath, the hold-up is blended back into the distillation residue. Weigh the distillation flask containing the residue and column hold-up (fraction boiling above 343°C (W_7g). Weigh the tared receiver containing the distillate (fraction boiling below 343°C (W_8) (note k).	(k) The fractions above and below 343°C may be examined in order to establish the identity of the oil.
	Calculations	
C7.12	(i) Calculate the percentage of water, C, in the pollutant as follows (note l): $C_1 = \frac{V_1}{W} \times 100\%_w$ (ii) Calculate the percentage of extraneous matter (insolubles) C_2, in the pollutant as follows: $C_2 = \frac{W_4 - W_3}{W_1} \times 100\%_w$ (iii) Calculate the percentage of oil, C_3, in the pollutant as follows: $C_3 = \frac{W_5 - W_2}{W_1} \times 100\%_w$ (iv) Calculate the percentage of the residue (>343°C) C_4, and distillate (<343°C) C_5 fractions and loss on distillation C_6 as follows:	(l) Taking the density of the water as one, V, ml weighs V_1g.

Step	Procedure	Notes

$$C_4 = \frac{W_7 - W_2}{W_5 - W_2} \times 100\%_w$$

$$C_5 = \frac{W_8 - W_6}{W_5 - W_2} \times 100\%_w$$

$$C_6 = \frac{(W_5 - W_2) - (W_7 - W_2) - (W_8 - W_6)}{W_5 - W_2} \times 100\%_w = \frac{W_5 - W_7 - W_8 + W_6}{W_5 - W_2} \times 100\%_w$$

D High Resolution Gas Chromatography

D0 Introduction

When a pollutant (oil, wax or tar) has been classified by low resolution gas chromatography (Method A), more precise classification may be obtained using high resolution gas chromatography (see Reference 8).

Classification may be obtained by examination of the features of the chromatogram produced and by comparison of those features to similar features obtained from oils of known character. The method is based on an Institue of Petroleum Method IP 318/73T (reference 1).

D1 Performance Characteristics

D1.1	Substances determined	Oils of petroleum origin (ie gasolines, kerosines, and diesel fuels), coal tar and its predominately neutral fractions. If the pollutant has been identified as one of a higher boiling range (eg crude oil, crude tar or fuel oil) by low resolution chromatography (Method A) then the fraction boiling below 343°C may be obtained by distillation (Method C).
D1.2	Type of Sample	Liquid petroleum oils, coal tar and its predominately neutral fractions, or solvent solutions of same.
D1.3	Basis of Method	High resolution gas chromatography and flame ionization detection on lower boiling distillate or pentane solution.
D1.4	Interference	Any compound in a given sample with a GC retention time within the ranges of the oil or tar present in that sample but not a component of the oil or tar.
D1.5	Time required for analysis	1.5 hours per chromatographic run.

D2 Principle

The oil or tar is characterized by programmed temperature gas chromatography using a capillary column. The individual compounds are separated approximately in order of boiling points and displayed on a chart from a recorder as a pattern of peaks, usually superimposed on an 'envelope' of a complex mixture of unresolved compounds, particularly for petroleum oils. The distinctive features of the pattern of peaks are used to characterize the oil.

The separation is achieved using a capillary column coated with OV101, OV1, SE52 or SE54. It is recommended that for inter-laboratory comparison a column should be used as specified by the Institute of Petroleum, viz. OV101. Where the pollutant is known to contain a significant fraction boiling above 343°C, the fraction boiling below 343°C can be separated by distillation if sufficient sample is avilable (Method C).

D3 Interference

Any compound in a given sample with a GC retention time within the range of the oil, or tar present in that sample but not a component of the oil, or tar will interfere, eg oil dispersants (reference 1).

D4 Hazards

The aromatic hydrocarbons should be handled with care because long term exposure might induce cancer. The solvents used are flammable and care should be taken to avoid sparks or naked flames during the preparation of standards etc.

D5 Reagents

Analytical or chromatographic grades are to be preferred where available.

D5.1 Selected n-paraffins up to nC_{20}, particularly C_8, C_{12}, C_{16}, C_{17}, C_{18}, C_{20}, and pristane and phytane[20].

D5.2 Indene, naphthalene, 1- and 2- methylnaphthalene, diphenyl, acenaphthene, dibenzofuran, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene and chrysene.

D5.3 It is suggested that typical samples of the following petroleum oils, tars and tar fractions and natural oils of known character be kept. Wherever possible, samples of oil type from more than one source should be available. The list given below is not comprehensive but represents possible pollutants. It must be borne in mind that the distribution and types of compounds occurring in samples can vary considerably, resulting in chromatograms of very different appearances. Thus, the use of reference samples is of quite limited value for characterization of samples from individual pollution incidents and the best comparisons are made between pollutant and suspected source materials (see Section D8).
Further information on characterization and the use of reference standards may be found in reference 1.

D5.3.1

Gasoline
Kerosine
White Spirt
Diesel fuel oil (35 secs)
Light residual fuel oil (approx. 220 secs)
Medium residual fuel oil (Approx. 960 secs)
Heavy residual fuel oil (approx. 3500 secs)
Non-soluble cutting oil
Light crude petroleum oil
Heavy crude petroleum oil

Reference samples of oils (particularly crude oils) may be obtained from Oil Pollution Division, Warren Spring Laboratory, Stevenage, Department of Trade and Industry.

D5.3.2

High temperature tar (coke oven tar)
Low temperature tar
Creosotes BS144 : 1973

Tars are commercially distilled into various fractions with boiling point ranges of 30°C to 100°C. Further details of these fractions can be found elsewhere (reference 2). Creosotes are blends of these fractions conforming to the relevant British Standard. In many cases fractions from the different types of tar (low and high temperature) are blended in various proportions to form creosotes.

If reference samples of coal tar and its products are required an approach should be made in the first instance to the Director and Secretary, British Tar Industry Association. 132/135 Sloane Street, London, SW1X 9BB.

D5.4 **Solvents:** Toluene, diethyl ether, and n-pentane.

D6 Apparatus

D6.1 **A gas chromatograph** capable of operating with capillary columns, fitted with a temperature programmer and flame ionization detector. A chart recorder is the best form of readout, set at a speed of 1 cm/min.

D6.2 **A stainless steel or, preferably, silica capillary column**
of 25–50 m length and 0.2–0.3 mm i.d. bore; for inter-laboratory comparisons reference columns should be used as specified by the Institute of Petroleum (see Section D2).

Step	Procedure	Notes
	Preparation of Instrument	
D7.1	Set up the instrument according to the manufacturer's instructions. The injection port heater and detector oven should be set at 300–350°C. The carrier gas should be helium set at a flow rate such that the resolution of nC_{17} and pristane is not less than 0.8 (see Notes a and b).	(a) Oxygen free nitrogen may also be used as a carrier gas but it must be passed through a deoxygenator. (b) Inject 1 µl of 1:1 mixture of nC_{17} and pristane (at a suitable concentration in toluene). The resolution should be greater than 0.8 under conditions as specified in Section D7.2.3. See low resolution GC method for details of how to measure resolution (see Method A)
D7.2	The initial and final programme temperatures and programme rate should be set according to the suspected nature of the sample as follows:	(c) Low boiling components can be better resolved by lower initial temperatures.

	Sample	*Initial Temp. (note c) °C*	*Final Temp. °C*	*Programme Rate °C/min.*
D7.2.1	Gasoline	30	150°	2
D7.2.2	Kerosine	55	200	5
D7.2.3	Diesel oil and 343°C fractions of heavier oils	100	225	5
D7.2.4	Coal tar and its neutral fractions	100	200	2

D7.3	Equilibrate the column at minimum oven temperature required and obtain a steady baseline (see note (d)). With some chromatographs it may be difficult to stabilize the oven at 30°C and, if so, the minimum possible stable oven temperature should be used.	(d) The column must have been previously stabilized by disconnecting the column from the detector and operating at 225°C overnight. Reconnect the column and programme over the working range to ensure that it has acquired stability. The sample size and sensitivity setting should be such that the pristane and phytane peaks if present are not less than 2 cm high and ideally the largest peak should be 90% full scale deflection.
	Sample Pretreatment	
D7.4	Where low resolution chromatography has indicated an oil with a maximum boiling point >343°C (ie higher boiling than diesel oil), the fraction boiling below 343°C can be obtained by distillation (Method C). The sample can also be extracted with n-pentane). (1 part sample to 9 parts n-pentane). This will precipitate some of the high molecular weight components (eg aspheltenes if present) which can be removed by filtration (see note e).	(e) This treatment may cause some change in the pattern of the chromatogram and should, be applied to the unkown sample, the standard oils and tars and suspected source materials.

Step	Procedure	Notes
	Gas Chromatography	
D7.5	Inject 1 µl of sample dissolved in a suitable solvent if necessary with an inlet splitter ratio between 40:1 and 100:1. A splitless injection technique may be used as appropriate for dilute solutions.	(f) Under conditions in D7.2.3 nC_{20} will be eluted in 32–34 mins.
	On injection, programme the temperature according to D7.2. Leave the column at maximum temperature until all the sample has eluted (see notes f and g).	(g) Under conditions in Appendix III phenanthrene will elute in 22–23 mins.
D7.6.1	Repeat this procedure for appropriate reference material and samples of individual n-alkanes, phytane and pristane in order to establish the identity of peaks in the sample.	
D7.6.2	Repeat this procedure for appropriate reference materials and solutions of the standards compounds in Section D5.2 in order to establish the identity of peaks in the sample.	(h) This figure can be used to characterize the sample. See section D8.2. (i) Where these peaks are superimposed on an envelope of unresolved compounds the baseline must be estimated (Ref. 9 Section 6).
D7.7	Measure the height of the pristane, and phytane peaks. Calculate the pristane to phytane ratio. (See notes h, i and j).	(j) The column should be checked regularly with reference materials, as it deteriorates with use.

D8 Characterization

D8.1 Samples of oil pollutant may be characterized by comparison of features of their gas chromatograms with those of typical known oils. However, because oil and tar types can vary widely in chromatographic nature the ability of the method to provide a precise characterization is often constrained by the number of typical oil samples available.

The analyst is advised to compile a comprehensive library of chromatograms and to have access to a wide range of typical oils and tars.

Oils isolated from pollution incidents can be mixtures or modified in nature primarily by loss of volatile components during weathering (reference 1). One of the most effective ways of using gas chromatograms is by comparison of the pollutant and suspected source material irrespective of the exact characteristics of either (see Reference 8).

D8.2 Examples of various petroleum oils are given in Appendix III. The most abundant peaks stand out from a broad envelope, those predominating being due to n-alkanes. The pristane to phytane ratio is to be taken as a guide only and variations of ± 10% in the ratio between sample and source material may be regarded as acceptable.

D8.3 Examples of various tars and creosotes are given in Appendix III. The most valuable features are:

D8.3.1 The boiling range of the sample

D8.3.2 The complexity of the pattern of components

D8.3.3 The relative amounts of the major components.

Coke oven tar and its fractions normally give patterns where the peaks due to unsubstituted aromatic hydrocarbons and heterocyclic compound (those listed in Section D5.2) predominate.

Low temperature tar and its fractions normally give more complex patterns with little or no predomination by peaks due to unsubstituted aromatic hydrocarbons.

E Identification of Gas Oil by the Isolation of the Chemical Markers

E0 Introduction

Statutory chemical markers are added to duty-free gas oils to distinguish these from DERV oils. These are quinizarin (1.75 mg l^{-1}) and furfuraldehyde (4 mg l^{-1})*. C.I. Solvent Red 24 (4 mg l^{-1}) is also used as a marker dye in gas oils and can be used as a visual aid for certain Premium Kerosines.

After low or high resolution g.c. analysis (Methods A and D), samples of oil isolated from pollution incidents are examined for quinizarin and C.I. Solvent Red 24, to enable gas oil to be identified.

*NB The use of furfuraldehyde was being discontinued in 1982.

E1 Performance Characteristics

E1.1	Substance determined	C.I. Solvent Red 24 and quinizarin.
E1.2	Types of Sample	Diesel oil is isolated from pollution samples, often in admixture with other oils.
E1.3	Basis of Method	Oil is extracted into petroleum spirit and passed down a Florisil column where the chemical markers are retained. C.I. Solvent Red 24 is eluted from the column with acetone and quinizarin with formic acid/acetone. The extracts are then applied to T.L.C. plates and developed, when the C.I. Solvent Red 24 appears as a pink spot and the quinizarin is visible under U.V. light.
E1.4	Range of Application (sample size)	Markers identified in 25 mg oil sample.
E1.5	Limit of Detection	50 ng quinizarin and 100 ng C.I. Solvent Red 24 (determined by practical observation of minimum visible quantities)
E1.6	Interference	Some degradation products from used lubricating oil may obscure the quinizarin spot. Statutory markers are also used in Regular Kerosine and C.I. Solvent Red 24 can be used as a visual aid for certain Premium Kerosines.
E1.7	Time Required for Analysis	45 minutes excluding extraction.

E2 Principle

After g.c. analysis, the gas oil is characterized by identification of the chemical markers. The oil is first extracted from the sample with 40° – 60° petroleum spirit, dried and then passed down a Florisil column. The column is then washed to give a residual oil which is weighed and may be subjected to further analysis.

The markers and other polar materials are retained on the Florisil column. The C.I. Solvent Red 24 is eluted with acetone, the quinizarin with formic acid/acetone and the extracts collected and evaporated. The residues are dissolved in acetone and applied to a T.L.C. plate together with suitable standards. The plate is developed, the C.I. Solvent Red 24 is visible as a pink spot and the quinizarin becomes visible under U.V. light (254 nm) (reference 7).

E3 Interferences

Whilst the chemical markers can occur in kerosines (see Section E1), the C.I. Solvent Red 24 is used at a much lower concentration. However, it must be noted that the technique is for application primarily with samples characterized previously as being diesel fuel oil (see Section E8).

E4 Hazards

The solvents used in the chromatography are flammable and care should be exercised to avoid sparks or naked flames during the preparation of the tanks and the procedure. The procedure should be carried out in a room with adequate ventilation and the acids handled with caution. Prolonged exposure to ultra-violet radiation can cause damage to eyes and if several determinations are carried out repetitively on a routine basis, it is advisable to wear suitable eye protection.

E5 Reagents

Analytical or chromatographic grades are to be preferred where available, but good laboratory grade will suffice for the solvents.

E5.1 **Solvents** Hexane, toluene, petroleum ether 40–60°.

E5.2 **Formic and acetic acids.**

E5.3 **Florisil** 60–100 mesh – heated for 2 hrs at 180°C (± 5°C) and store in a dessicator over silica gel.

E5.4 **Silica Gel G.** thin layer stationary phase, precoated 0.25 mm layer plates may be purchased.

E5.5 **Quinizarin** (1,4 – dihydroxyanthraquinone).

E5.6 **C.I. Solvent Red 24.**

E5.7 **Hydrochloric Acid.**

E5.8 **Anhydrous Sodium Sulphate**

E5.9 **Gas oil** (ordinary commercial grade)

E6 Apparatus

E6.1 **Bottle roller.**

E6.2 **Glass column** 20 mm × 10 mm

E6.3 **20 µl micropipette.**

E6.4 **Glass plates** where necessary

E6.5 **T.L.C. development tank.**

E6.6 **U.V. lamp unit** with 254 nm lamp.

E6.7 **Preparation of Chromatography Column.**

Plug the column with a small piece of cotton wool. Add 0.5 gm. of Florisil with tapping, Wash with 20 ± 2 ml of 40° – 60°C petroleum spirit.

E7 Sample Storage

Sample bottles should be glass and sealed with a PTFE lined stopper.

E8 Analytical Procedure

Step	Procedure	Notes
	Extraction of oil	
E8.1	To approximately 1 litre of water sample (see notes a and b) in a 1150 ml (40 oz) bottle add sufficient conc. hydrochloric acid to adjust the pH to 2. Add 25 ± 2 ml of 40° – 60°C petroleum spirit, seal with a PTFE-lined stopper and roll on electrically driven rollers for 1 hour, alternatively the sample may be shaken for 5 mins. (risk of emulsion formation). Distilled water is added to raise the solvent layer into the neck of the bottle and the upper layer is carefully pipetted off. This is then dried with 2g anhydrous sodium sulphate.	(a) Where approx 500 mg of the oil may be removed from the surface without difficulty the extraction step may be ignored. (b) For oil samples already prepared in toluene or diethyl ether, the solvent should be removed by evaporation and the sample redissolved in 40° – 60°C petroleum ether.
	Isolation of Markers	
E8.2	Pass the petroleum spirit extract (see note c) down a Florisil Column (prepared as in E6.7) and wash the column with 20 ± 2 ml of 40° – 60°C petroleum spirit. Evaporate the bulked eluates to give a residual oil. Weigh the residue (see notes d and e).	(c) Alternatively between 25 & 500 mg of the oil itself may be dissolved in 25 ml of 40° – 60°C petroleum spirit, dried with sodium sulphate as in 7.1 and then passed down the Florisil column. (d) The oil may then be subjected to further analysis to identify the type. (e) The hydrocarbon markers are retained on the Florisil column together with other polar material which interfere with the identification of quinizarin.
	Separation of Chemical Markers	
E8.3	Elute the C.I. Solvent Red 24 from the Florisil column by passing 5 ± 1 ml of acetone down the column; collect the eluate. Wash the column with 20 ± 2 ml of acetone and discard these washings. (see note f).	(f) This removes some of the polar compounds.
	Chromatography	
E8.4	Evaporate the eluates to dryness and dissolve the residues each in 20 ± 2 µl of acetone. Apply these entirely to a glass T.L.C plate coated with Silica Gel using a 20 µl pipette. Apply individually 0.2 µg of C.I. Solvent Red 24 and 0.1 µg of quinizarin, both dissolved in acetone, as standards (see note g).	(g) If only a small quantity of oil is isolated and there is some doubt as to the presence of these markers, a similar quantity of reference marked gas oil may be run through the procedure from E7.2 in order to demonstrate whether identification of the markers is possible. If the isolate contains coloured material from the original sample it may be necessary to use more than 20 µl. For very thin layered plates 0.02 µl of Solvent Red and Quinizarin give better spots.
E8.5	Prepare and equilibrate a tank containing 15:15:1 hexane : toluene: acetic acid (all v/v) to a depth of 1 cm (see another Publication (9) in this series). Develop the plate (10 cm has been found to be a suitable development distance).	

Step	Procedure	Notes
	Identification	
E8.6	After development and thorough drying C.I. Solvent Red 24 will appear on the plate as a pink spot Rf. 0.4 and quinizarin appears when viewed under a U.V. light as a yellow fluroescent spot Rf 0.6 (see note h). Where used lubricating oil is present, the quinizarin may be obscured.	(h) Visualization of the quinizarin is improved in a dark room.

E9 Characterization

Gas oil may be identified from the presence of the chemical markers, particularly C.I. Solvent Red 24. Although these markers are present in certain kerosines, the procedure has been designed to apply primarily to diesel fuel oils which would have been characterized previously by gas chromatography. If the gas oil is present in a mixture of known composition, say of gas and derv oils, then an approximate estimation may be obtained by preparing standard mixtures and subjecting these to the procedure. The proportion of gas oil may be deduced by comparing the intensities of standard and sample chromatographic spots.

Appendix I

Typical Low Resolution Gas Chromatograms for Method A Prepared by the Laboratory of the Government Chemist

Operating Conditions

Initial temperature	– 100°C
Final temperature	– 300°C
Injector temperature	– 325°C
Detector temperature	– 325°C
Programme rate	– 5°C Min^{-1}
Chart speed	– 10 mm Min^{-1}
Columns	– Stainless Steel 1 metre lengths and 3 mm ID packed with 5% OV-1 on diatomite M-AW-DMCS 80–100 mesh
Gas	– Nitrogen 25 mls min^{-1}
Gas chromatograph	– PERKIN ELMER sigma 3
Recorder	– BRYANS 28000 (10mV full scale deflection)

Reference Chromatograms in Appendix I

	Fig.		Fig.
Kuwait Crude Oil	18	Used nonsoluble cutting oil	28
North Sea Crude Oil (Beatrice)	10	High temperature coke oven tar	19
Crude Oil Cargo Tank Residues	21	Low temperature coke oven tar	15
Gasoline (two samples)	13, 26	Creosote blended (high and low temperature tars)	9
Gas Oil	17	Creosote blended (high temperature tars)	29
Kerosine (two samples)	16, 24	Creosote blended (low temperature tars)	31
Light Fuel Oil	30	Refined Sunflower Oil (two samples)	12, 25
Medium Fuel Oil (in chloroform)	27	Rapeseed Oil	22
Heavy Fuel Oil (in chloroform)	23	Coconut Oil (in chloroform)	8
White Spirit	20	Palm Kernel Oil (in chloroform)	7
Transformer Oil	14		
Lubricating Oil	11		

Figure 7 PALM KERNEL OIL IN CHLOROFORM

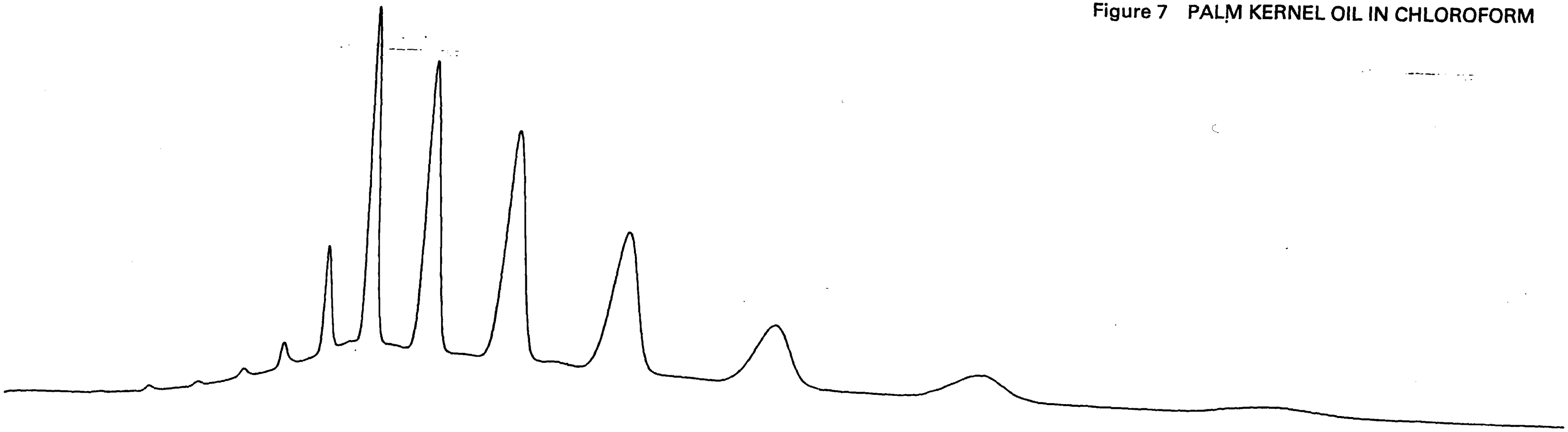
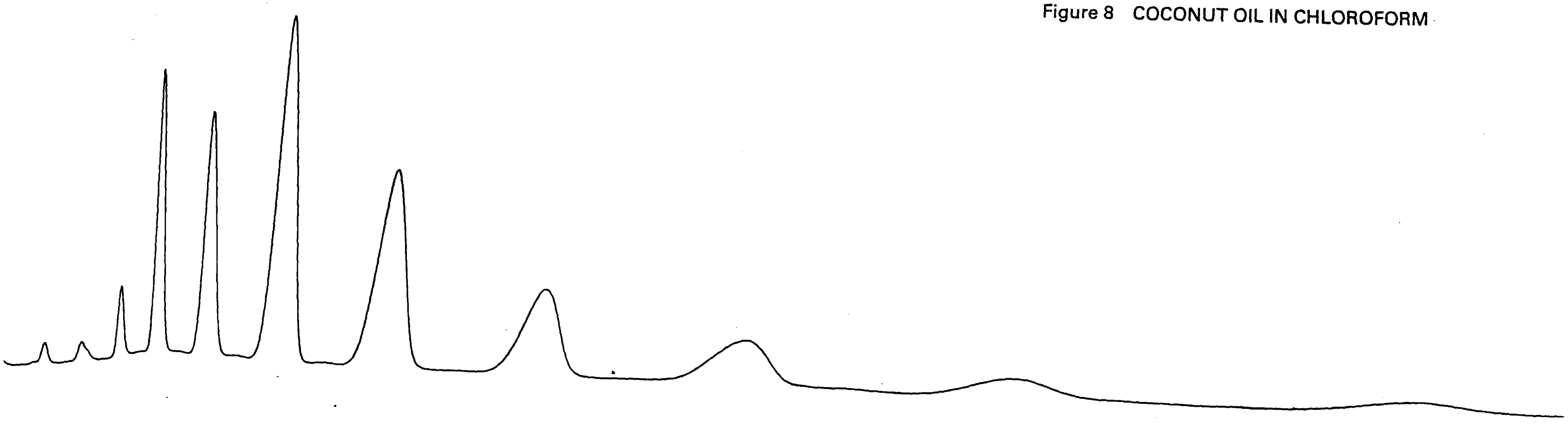


Figure 8 COCONUT OIL IN CHLOROFORM



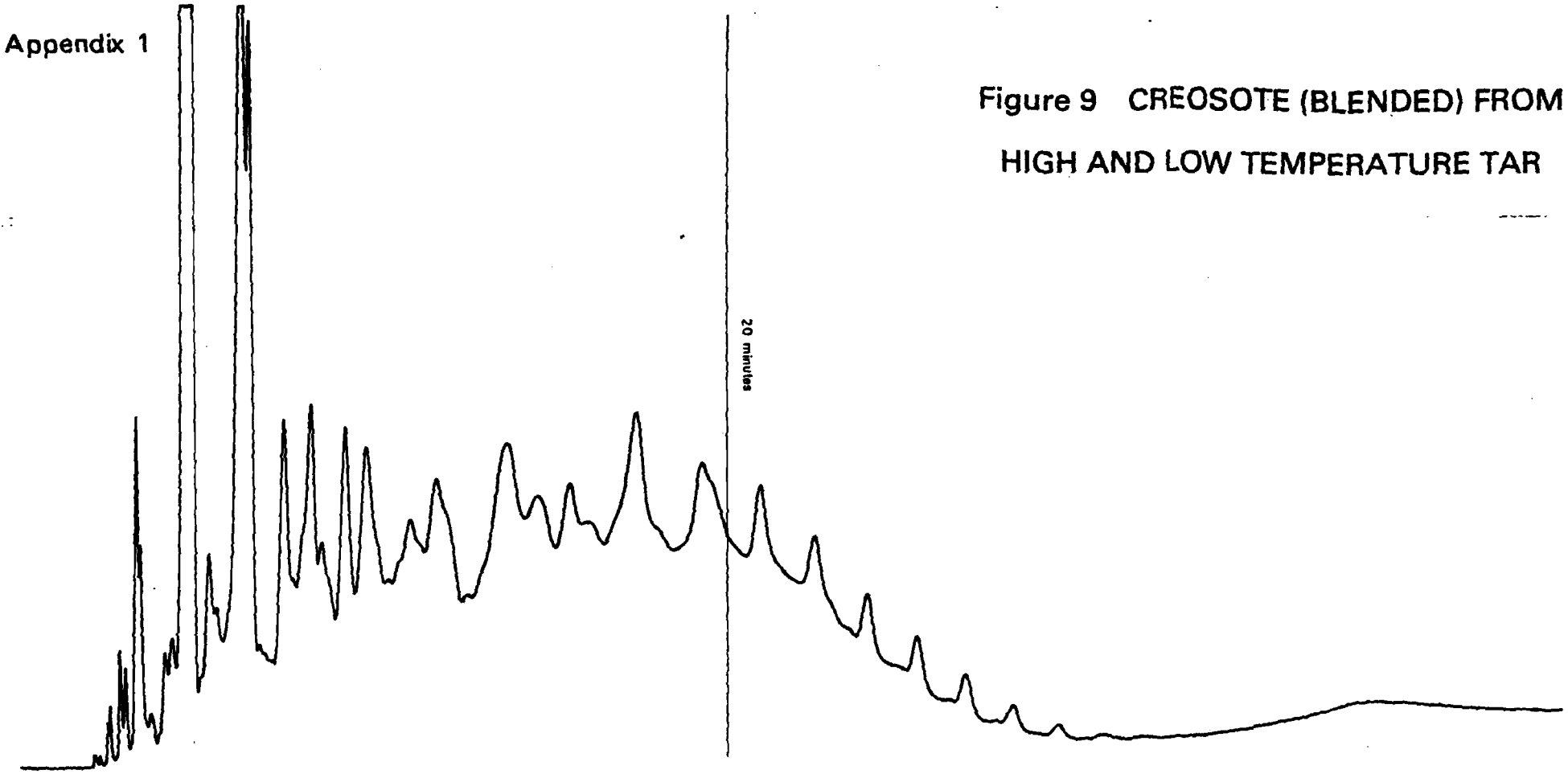
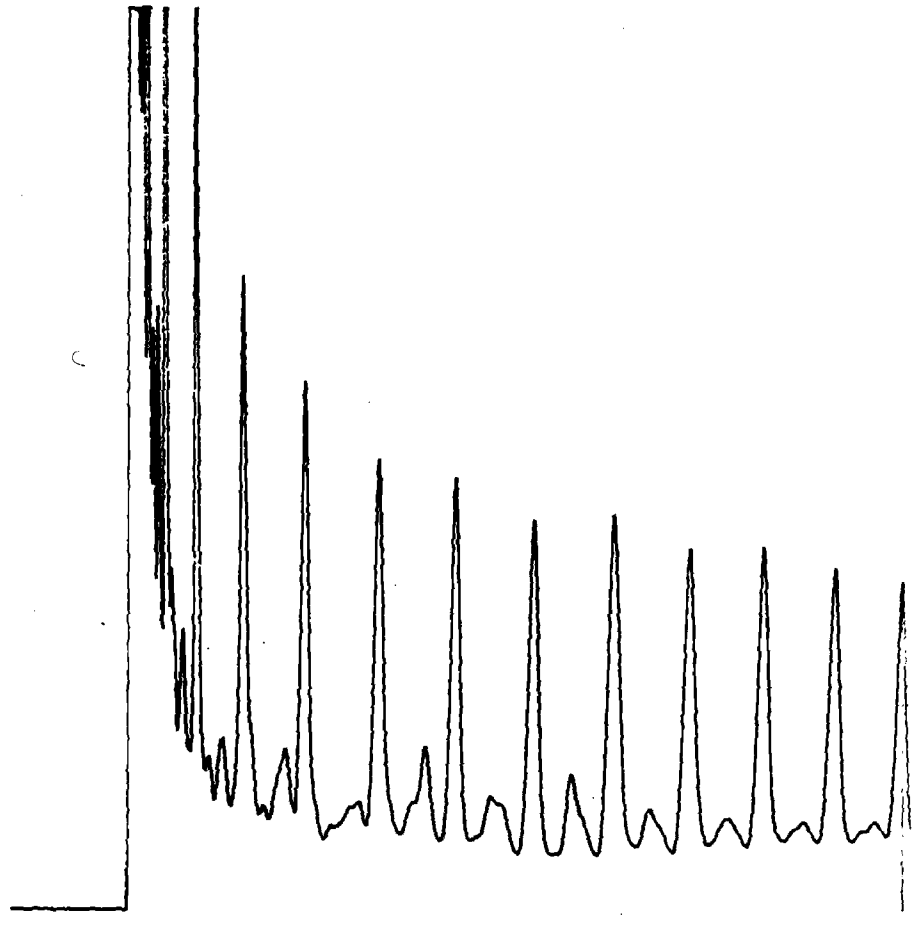


Figure 9 CREOSOTE (BLENDED) FROM HIGH AND LOW TEMPERATURE TAR



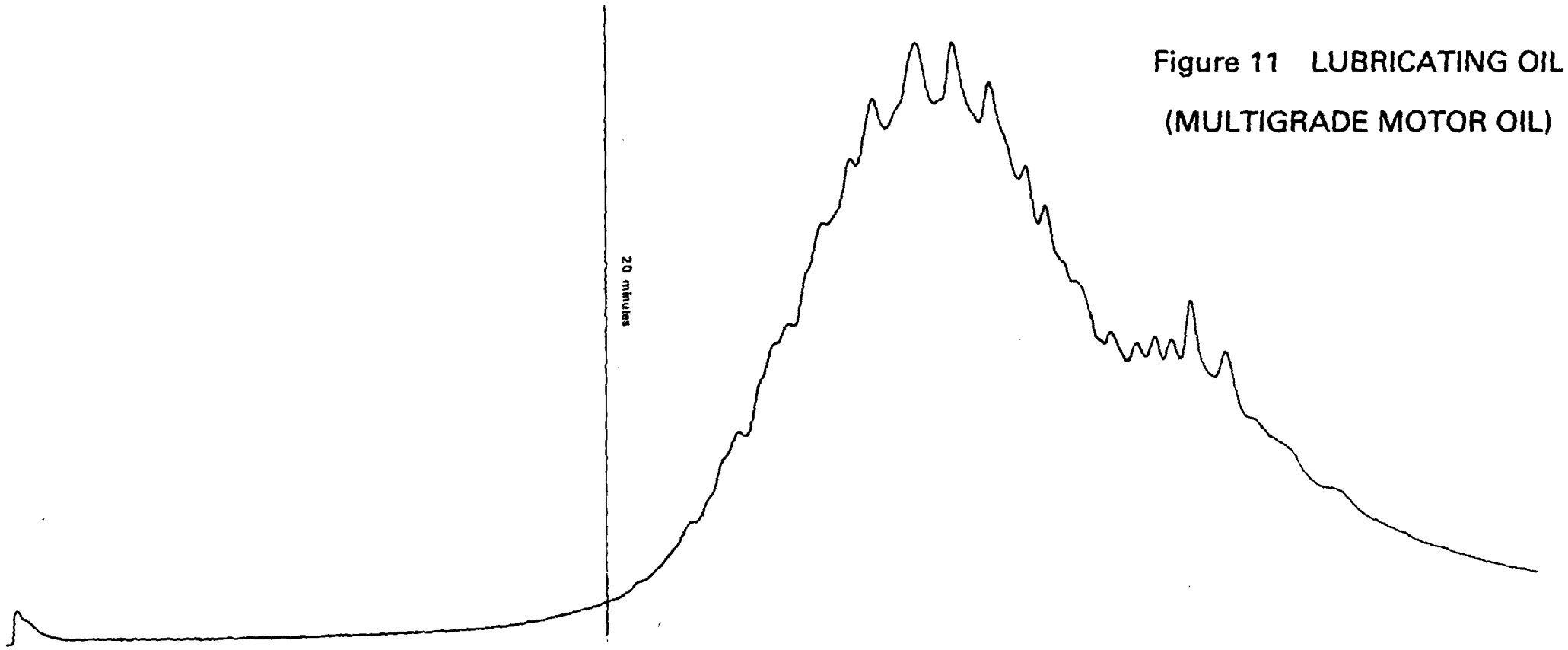


Figure 11 LUBRICATING OIL (MULTIGRADE MOTOR OIL)

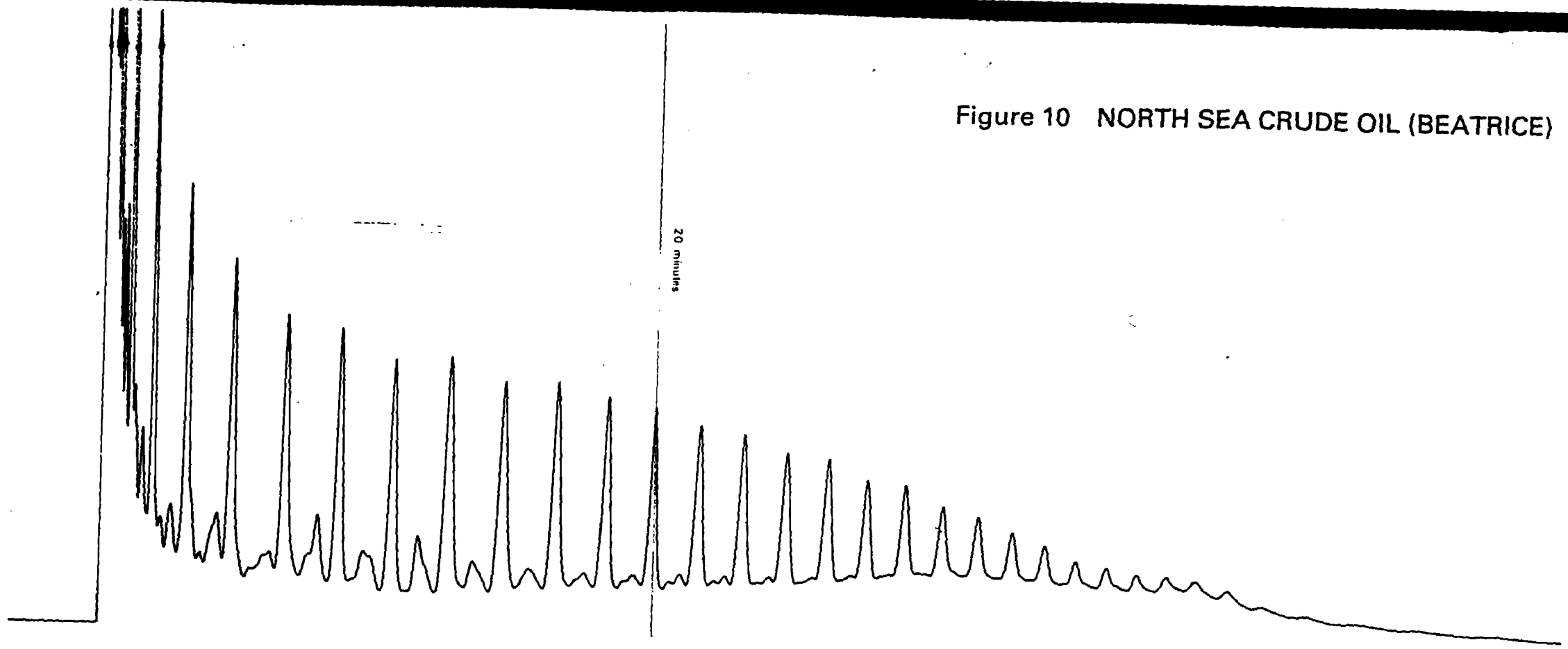
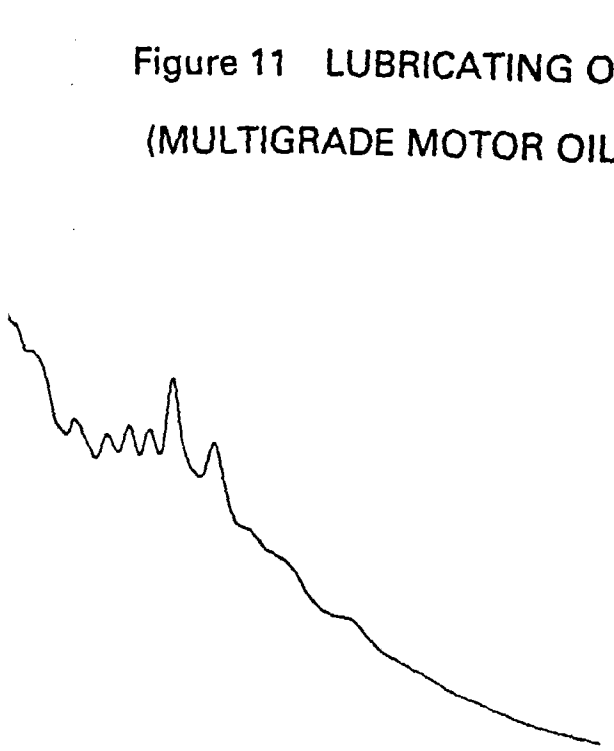


Figure 10 NORTH SEA CRUDE OIL (BEATRICE)

Figure 11 LUBRICATING OIL
(MULTIGRADE MOTOR OIL)



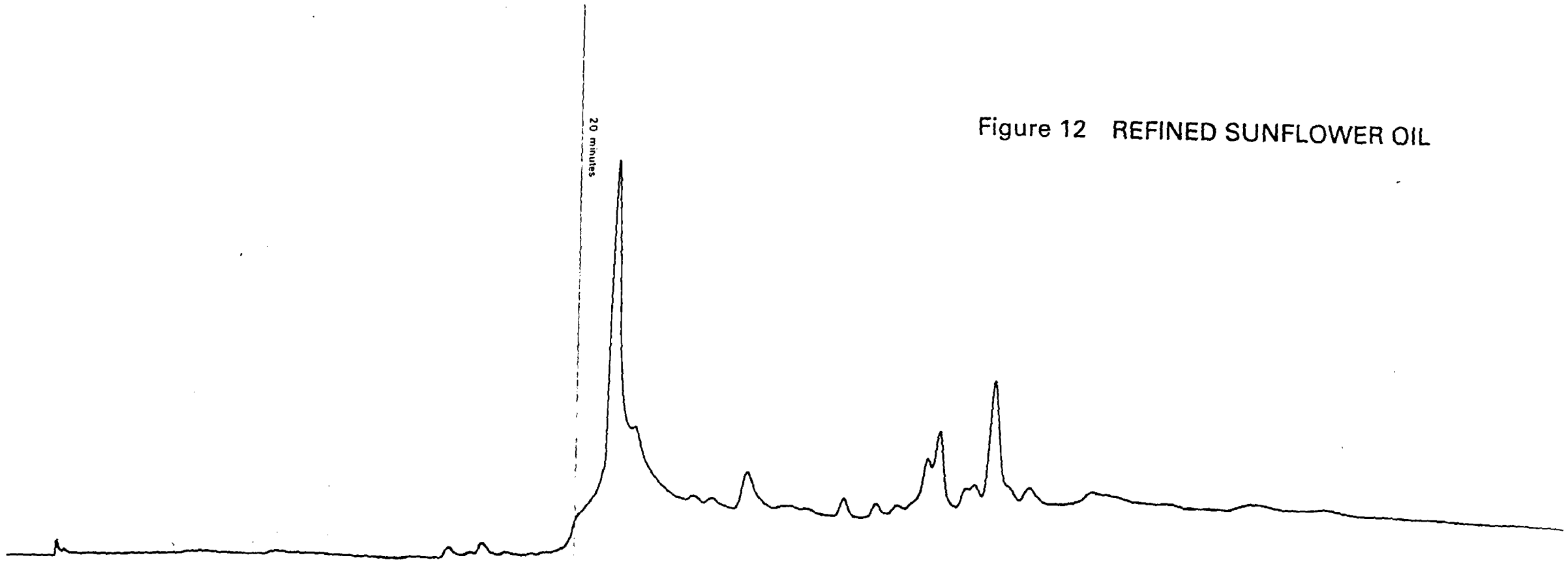


Figure 12 REFINED SUNFLOWER OIL

Appendix 1

Figure 13 GASOLINE

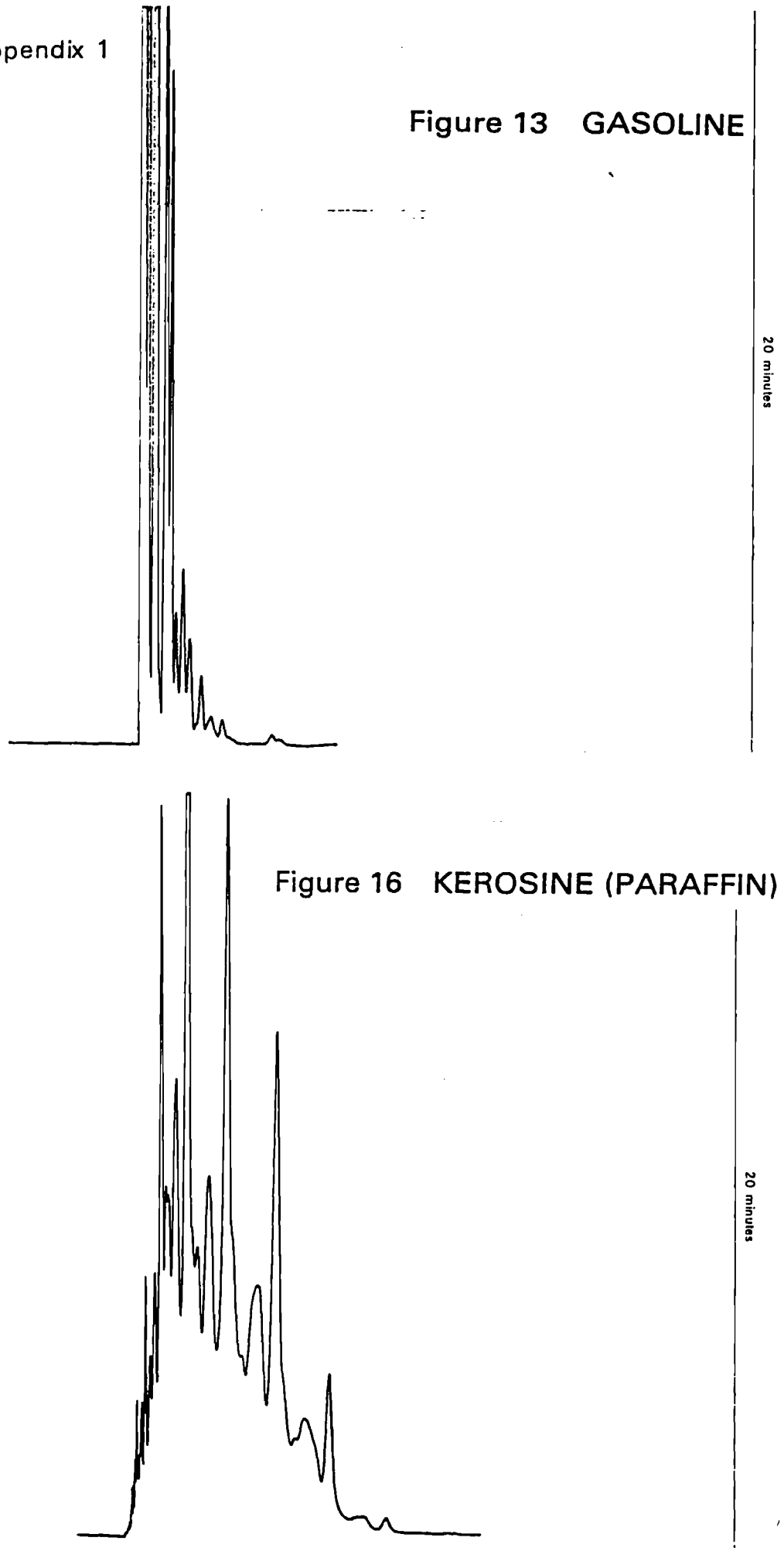


Figure 14 TRANSFORMER OIL

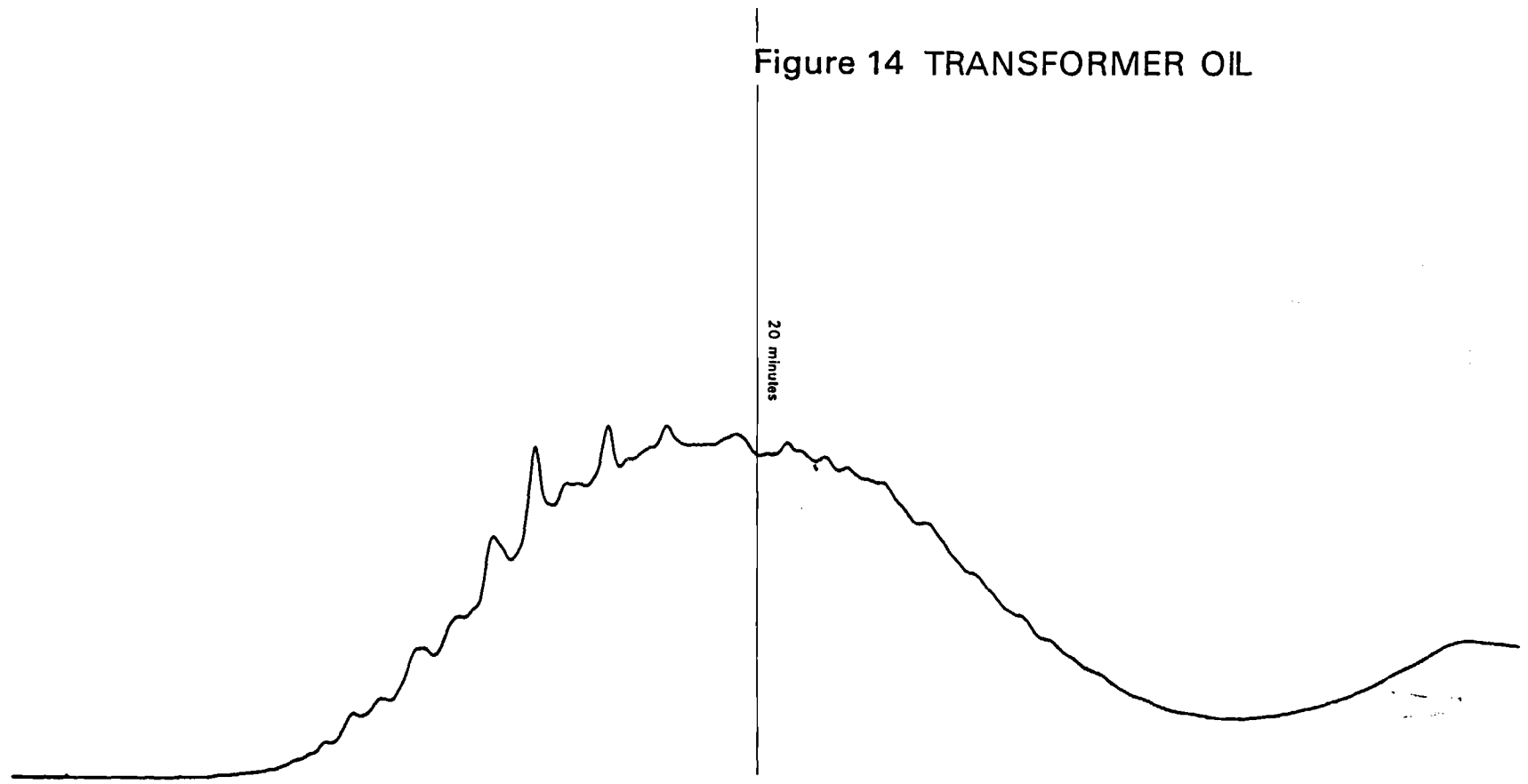


Figure 16 KEROSINE (PARAFFIN)

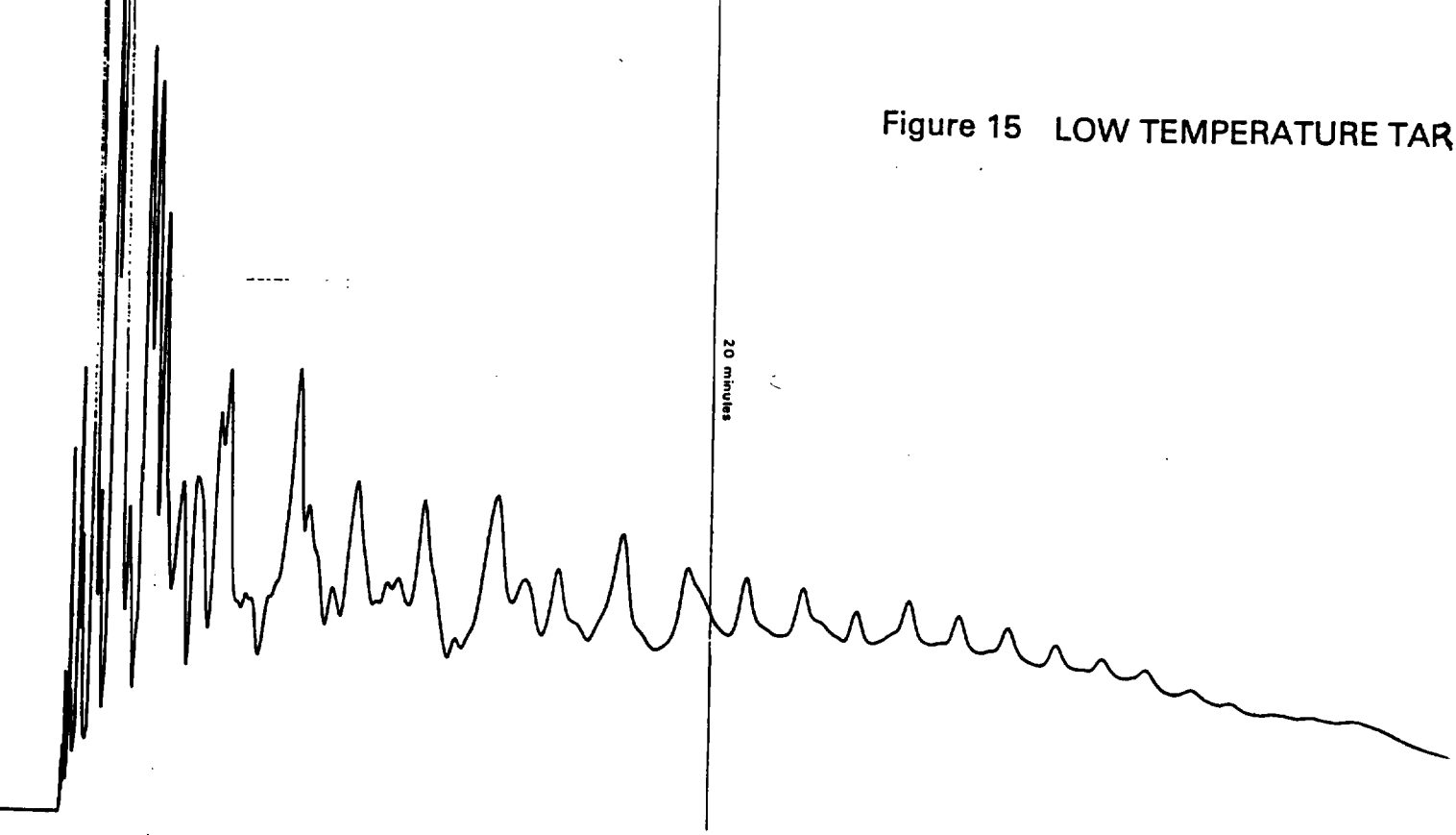


Figure 15 LOW TEMPERATURE TAR

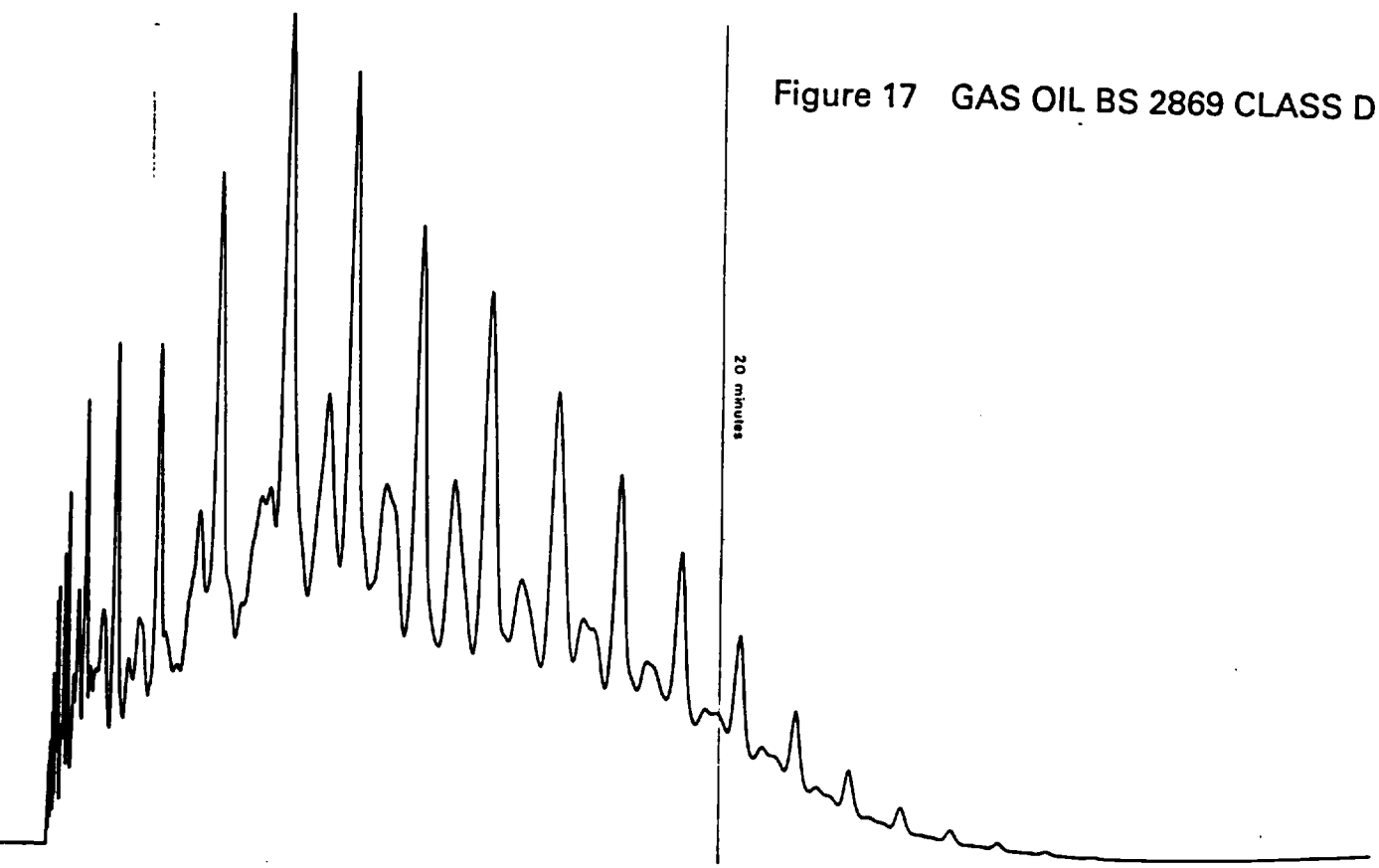


Figure 17 GAS OIL BS 2869 CLASS D

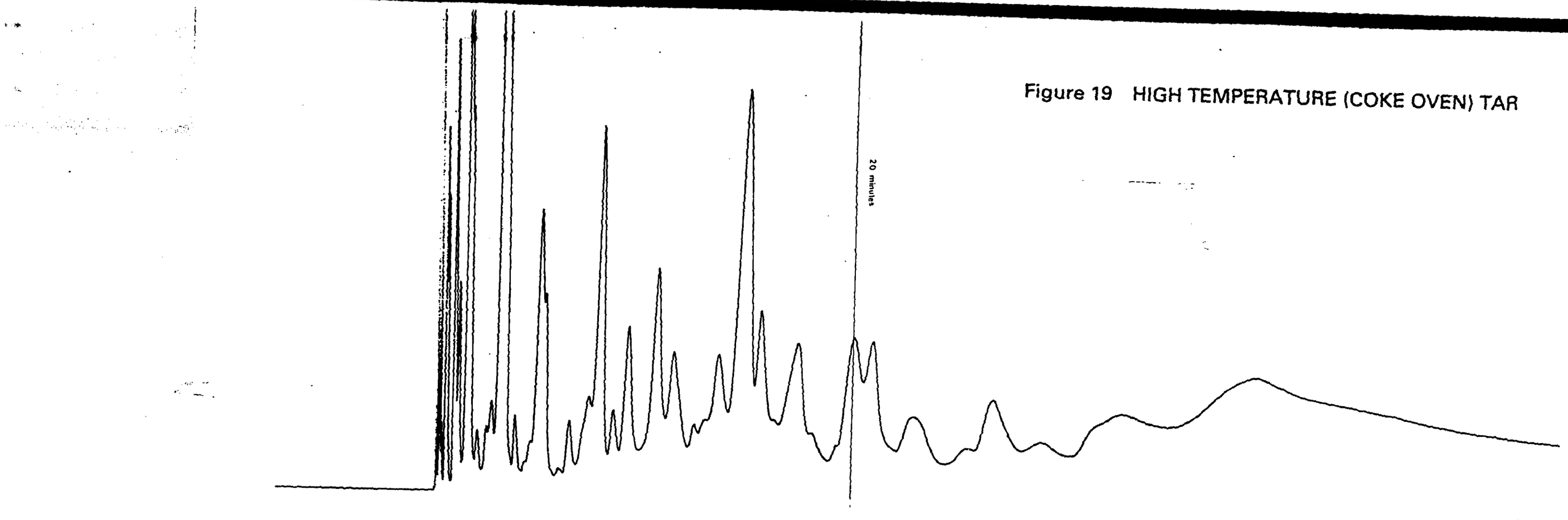


Figure 19 HIGH TEMPERATURE (COKE OVEN) TAR

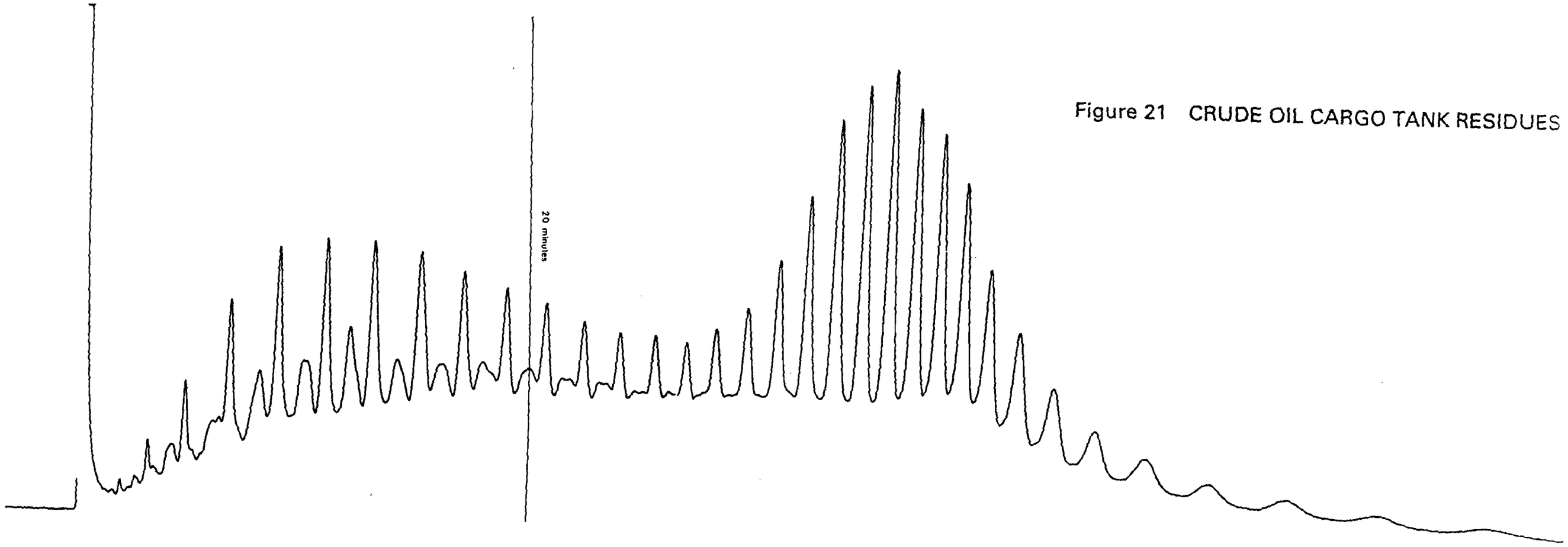


Figure 21 CRUDE OIL CARGO TANK RESIDUES

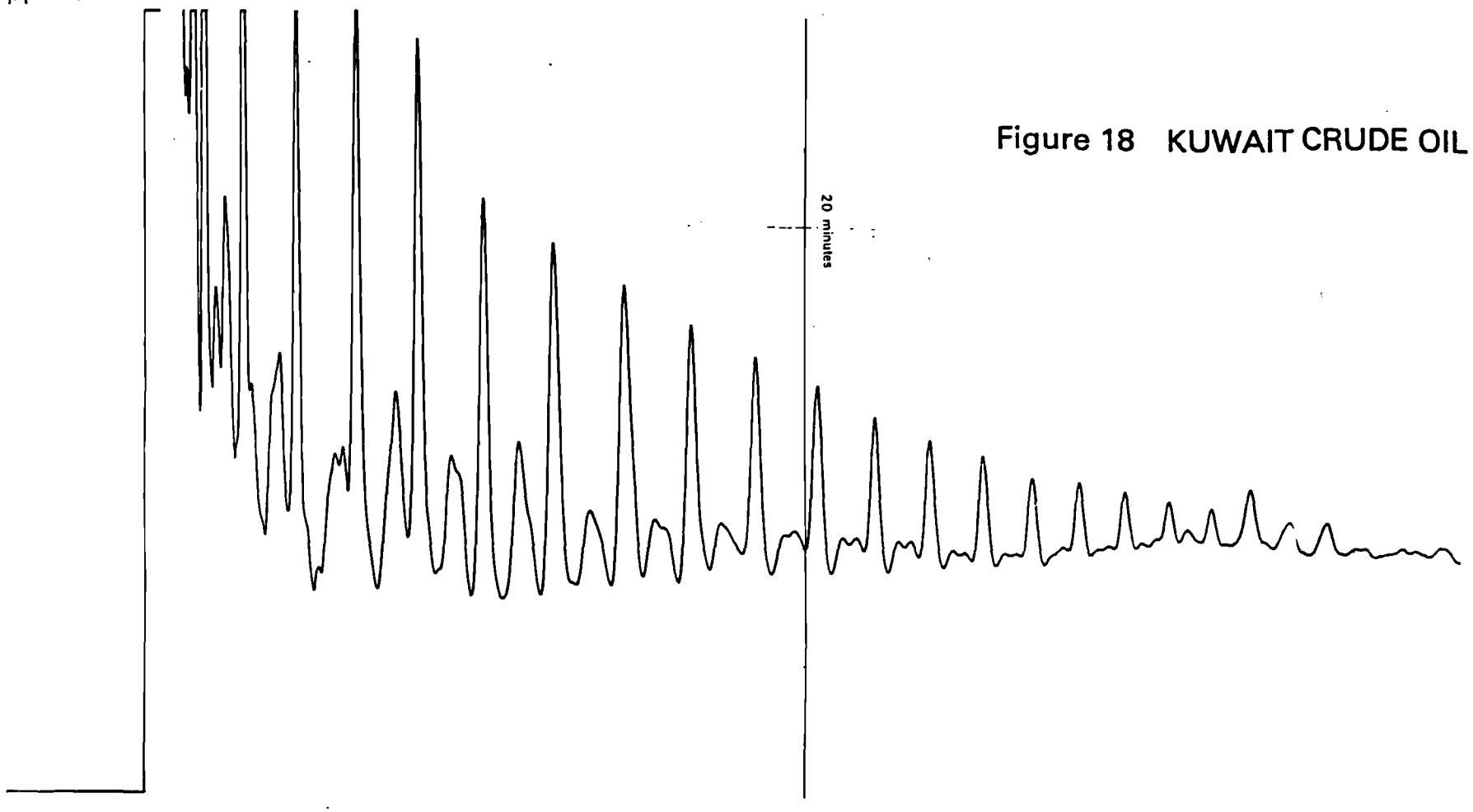


Figure 18 KUWAIT CRUDE OIL

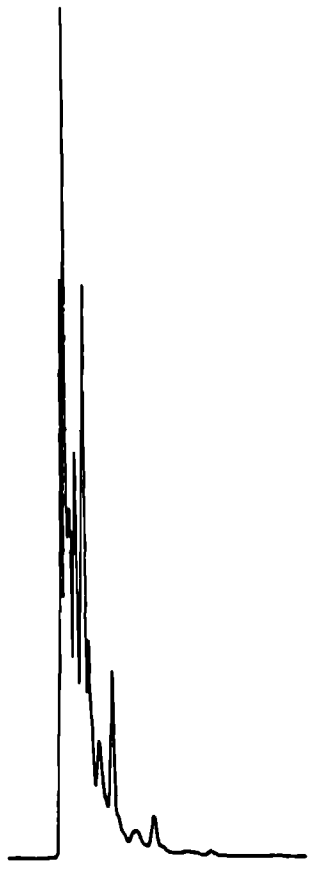


Figure 20 WHITE SPIRIT

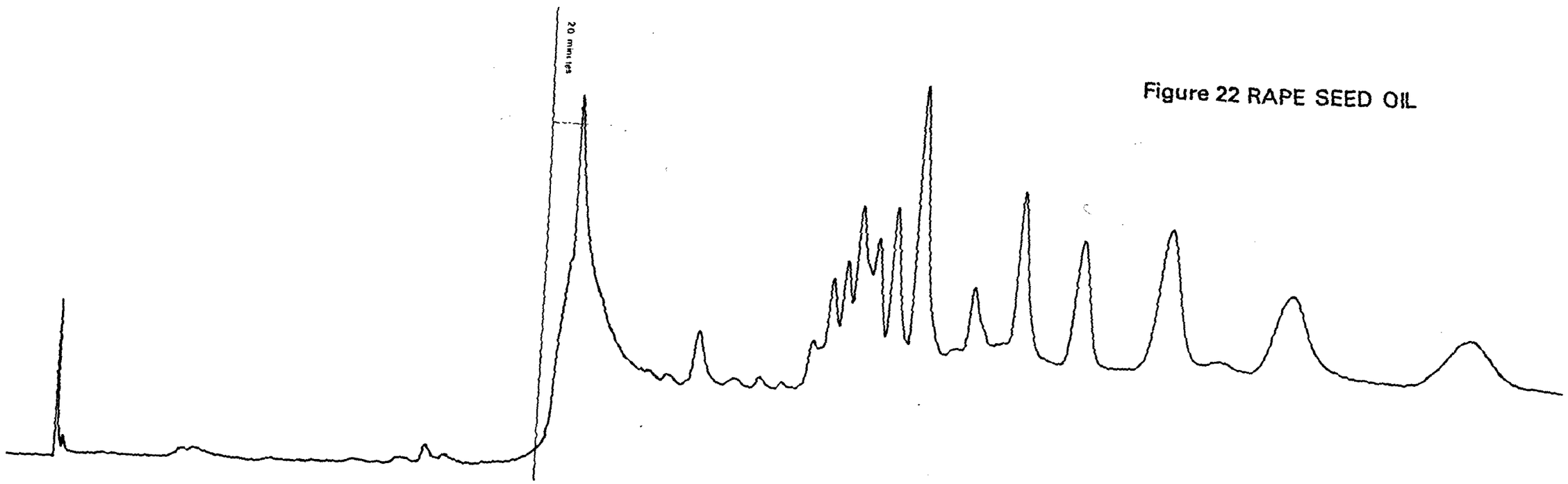


Figure 22 RAPE SEED OIL

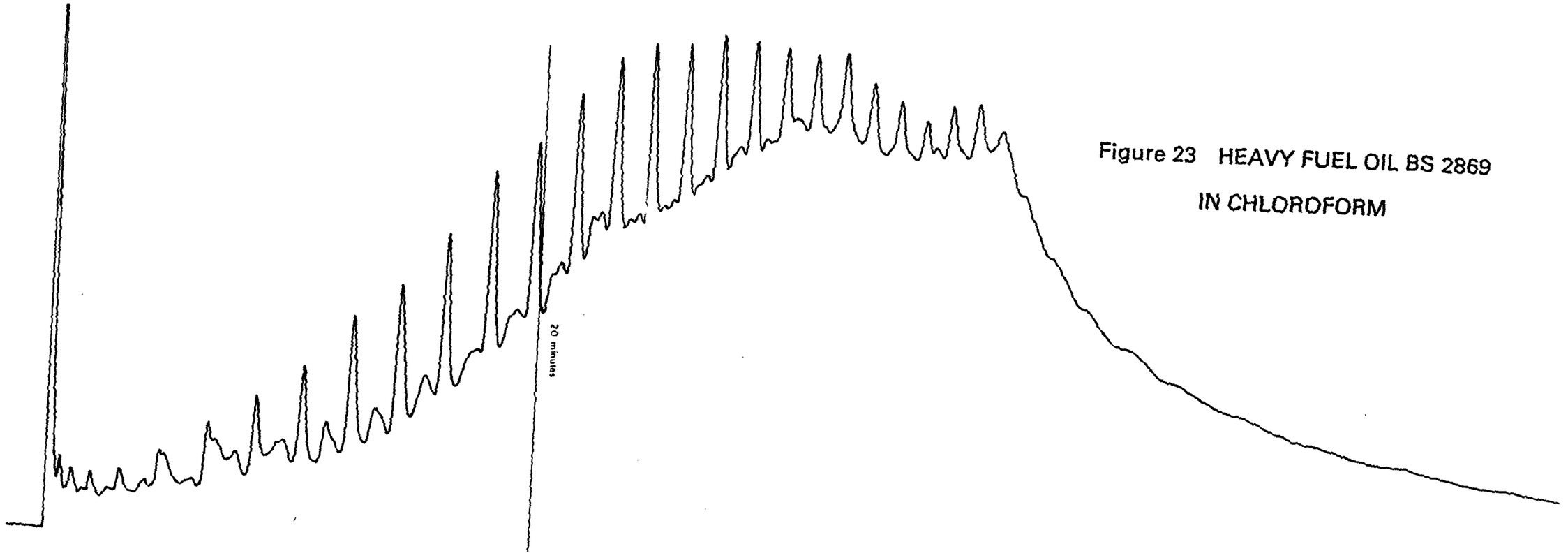


Figure 23 HEAVY FUEL OIL BS 2869
IN CHLOROFORM

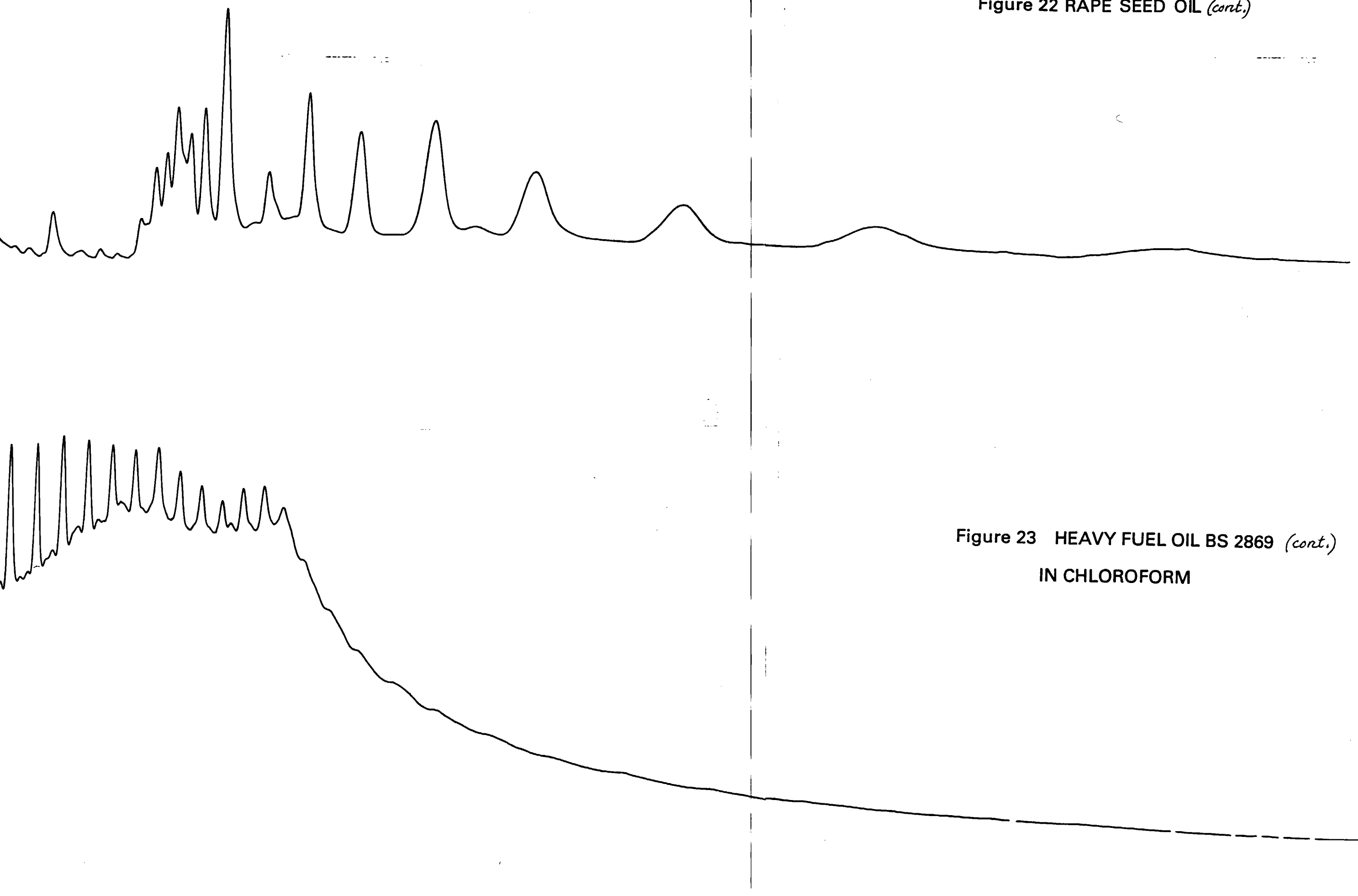


Figure 22 RAPE SEED OIL *(cont.)*

Figure 23 HEAVY FUEL OIL BS 2869 *(cont.)*

IN CHLOROFORM

Figure 24 KEROSINE

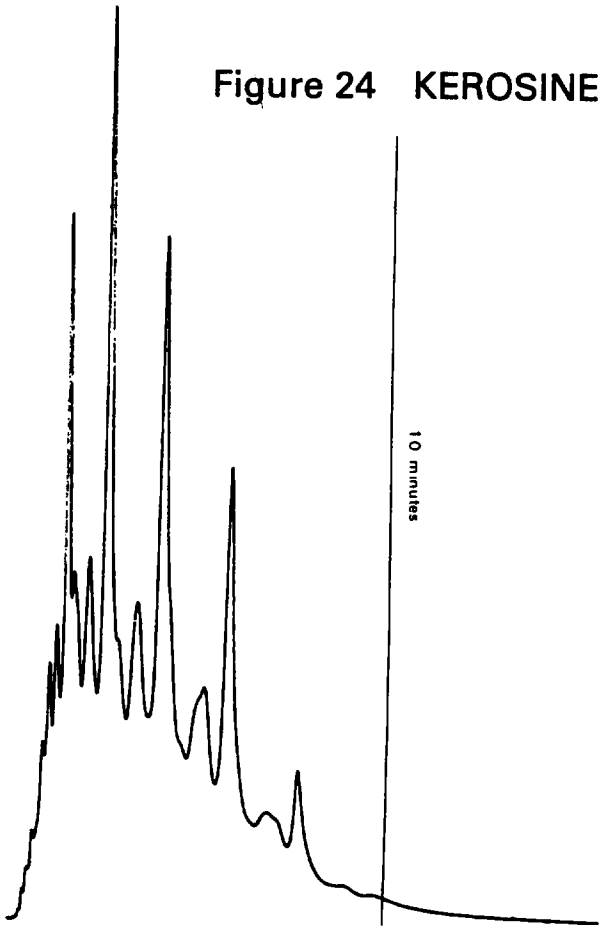
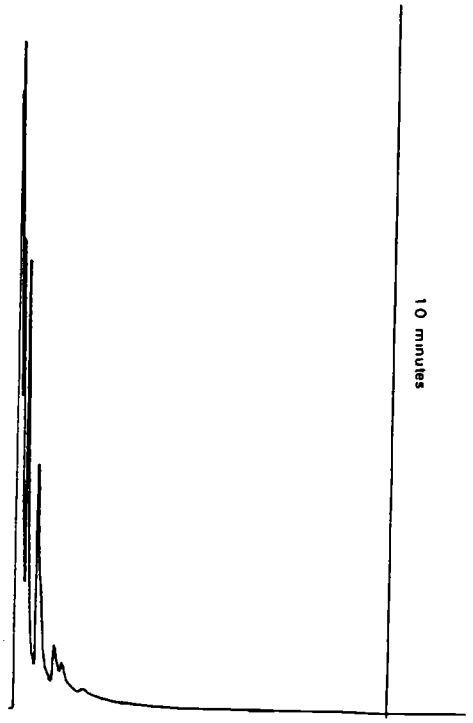


Figure 26 GASOLINE



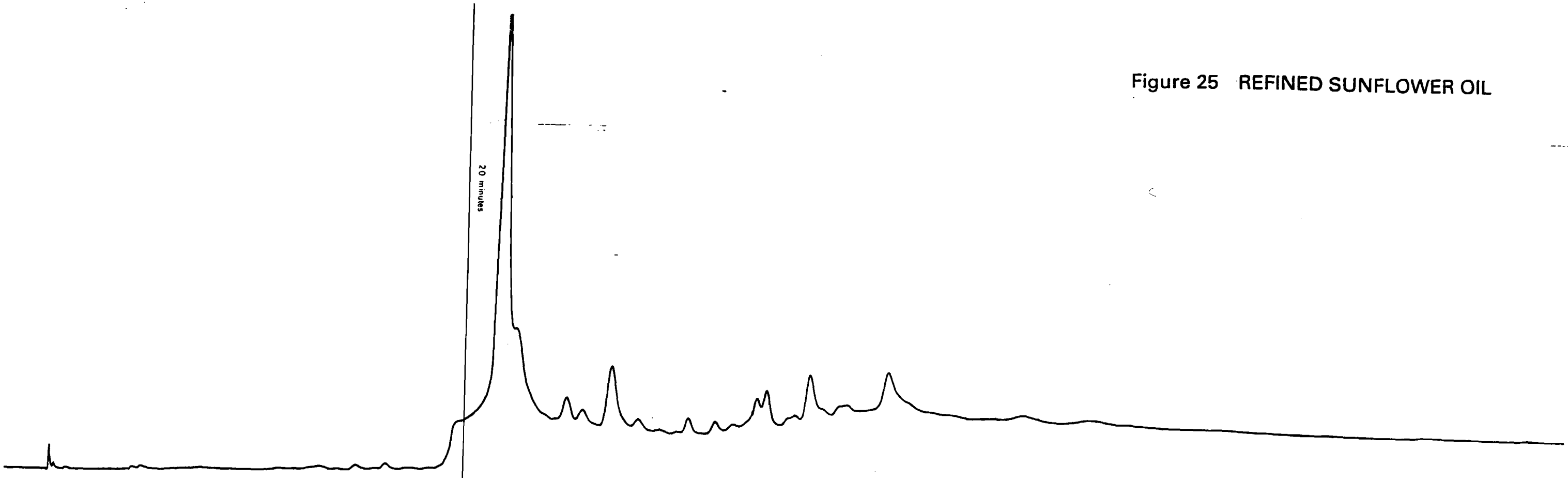


Figure 25 REFINED SUNFLOWER OIL

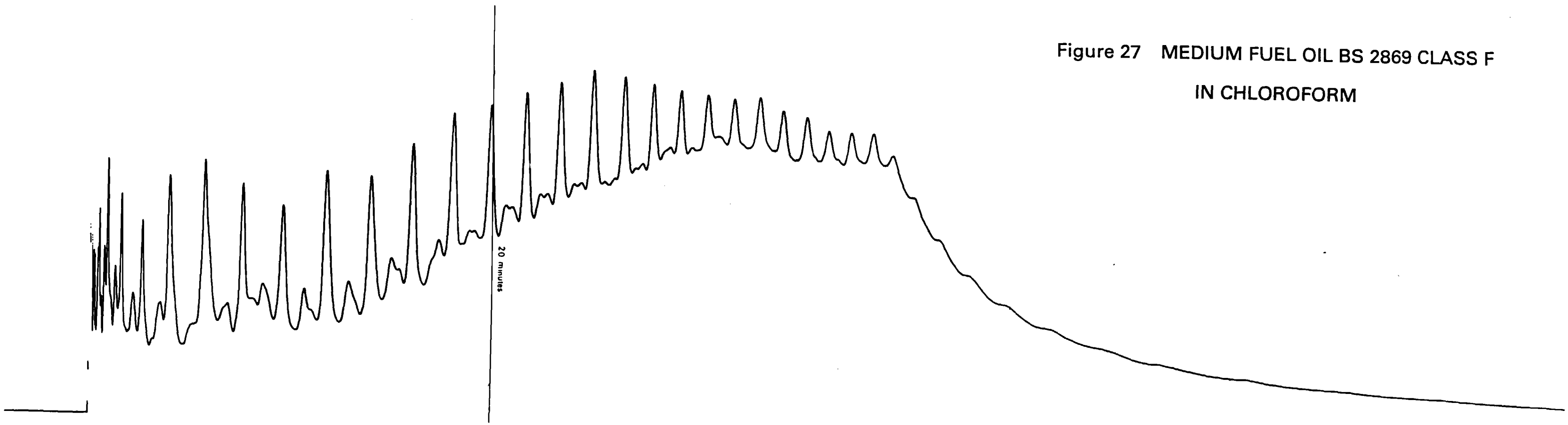


Figure 27 MEDIUM FUEL OIL BS 2869 CLASS F
IN CHLOROFORM

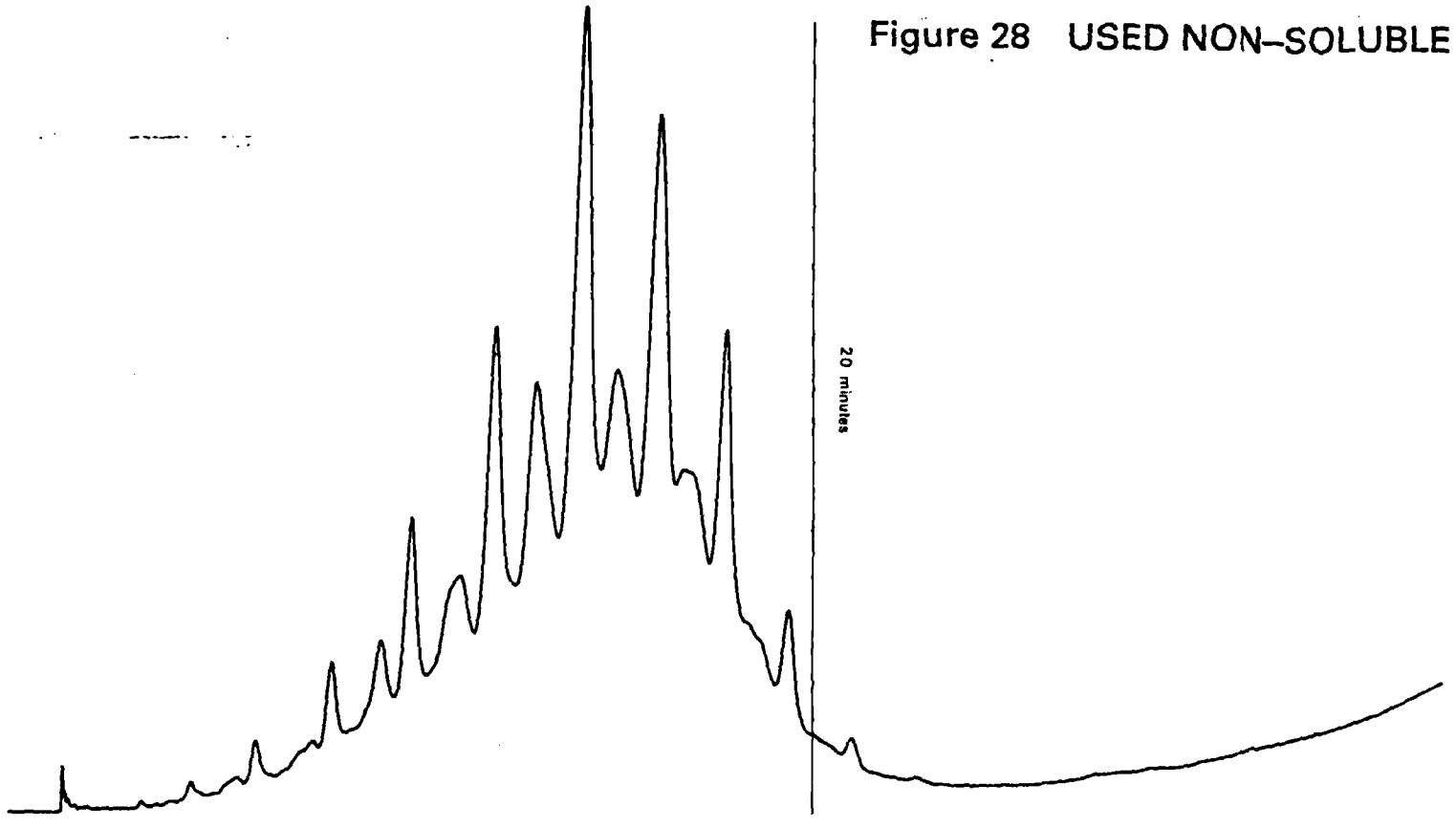


Figure 28 USED NON–SOLUBLE CUTTING OIL

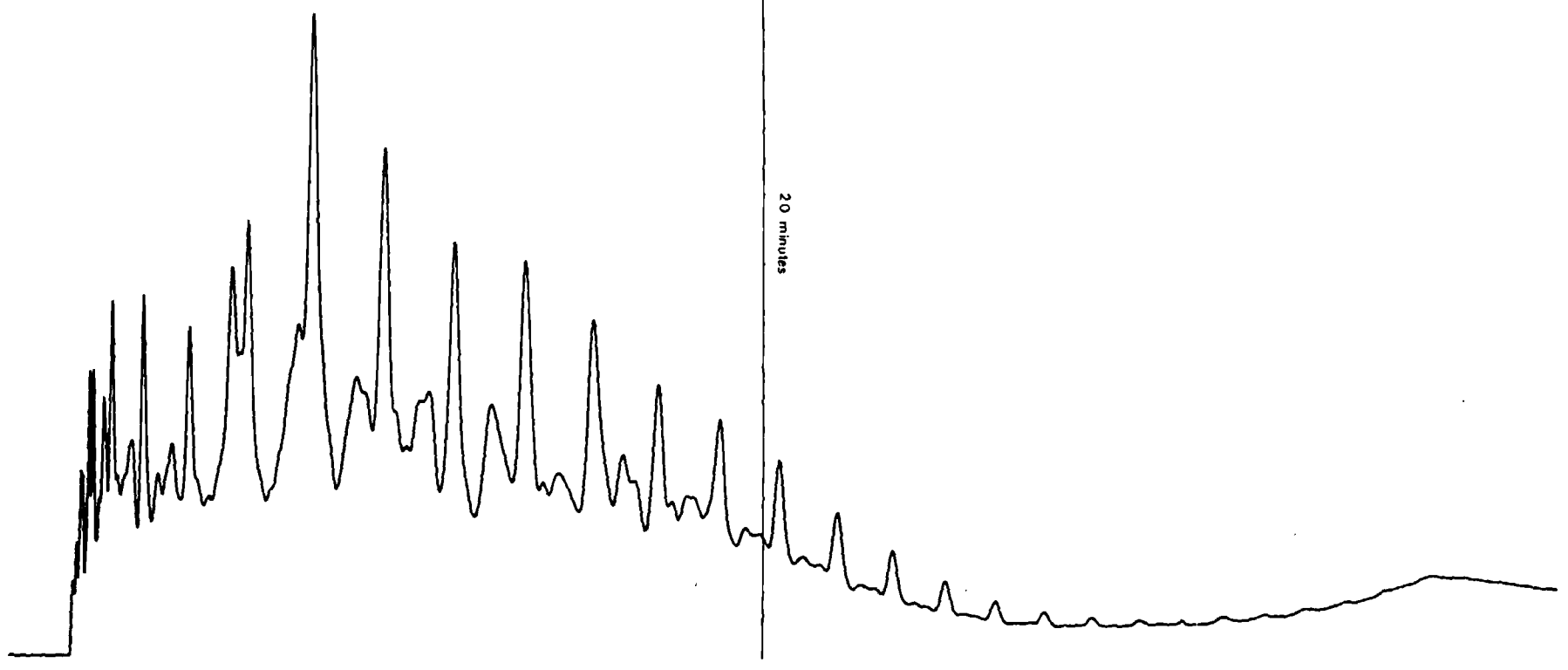


Figure 30 LIGHT FUEL OIL BS 2869 CLASS E

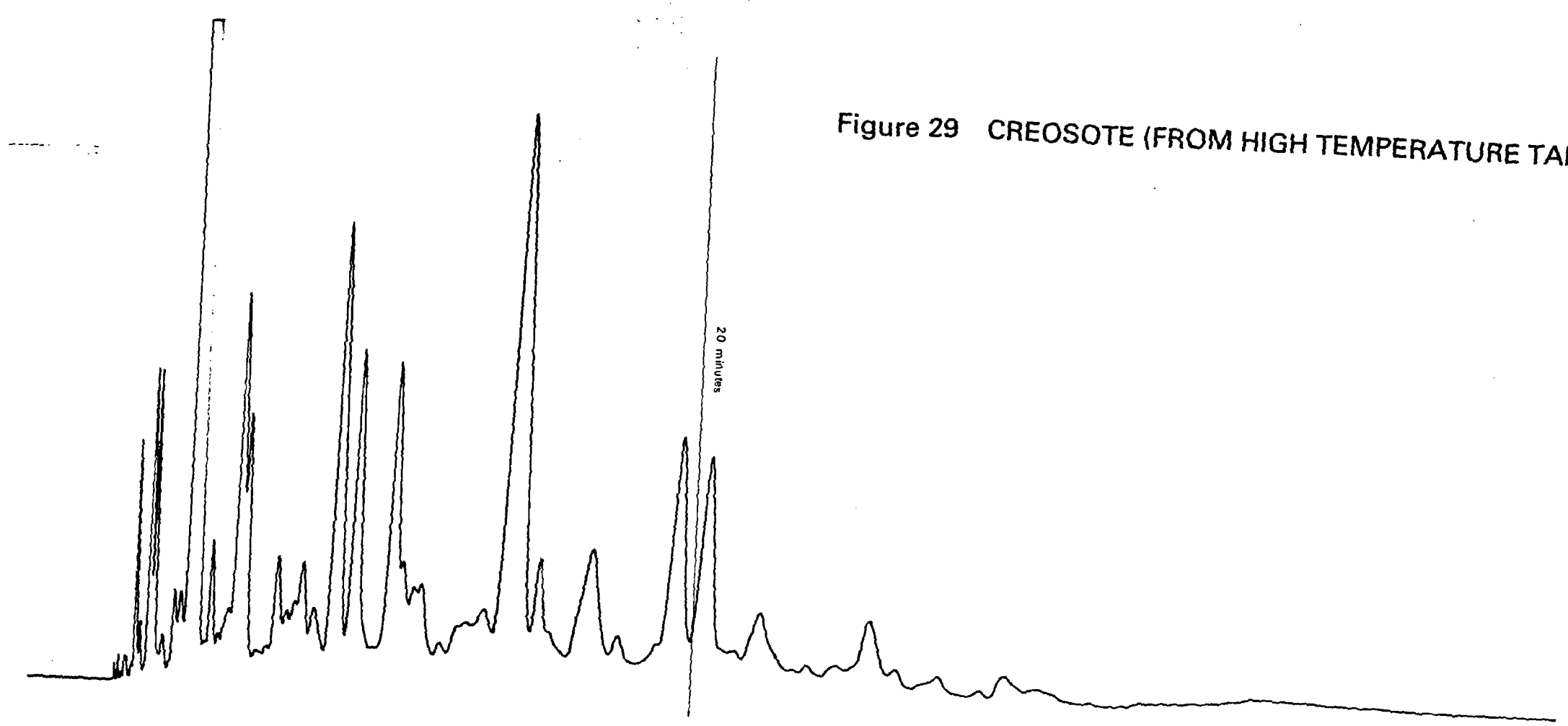


Figure 29 CREOSOTE (FROM HIGH TEMPERATURE TAR)

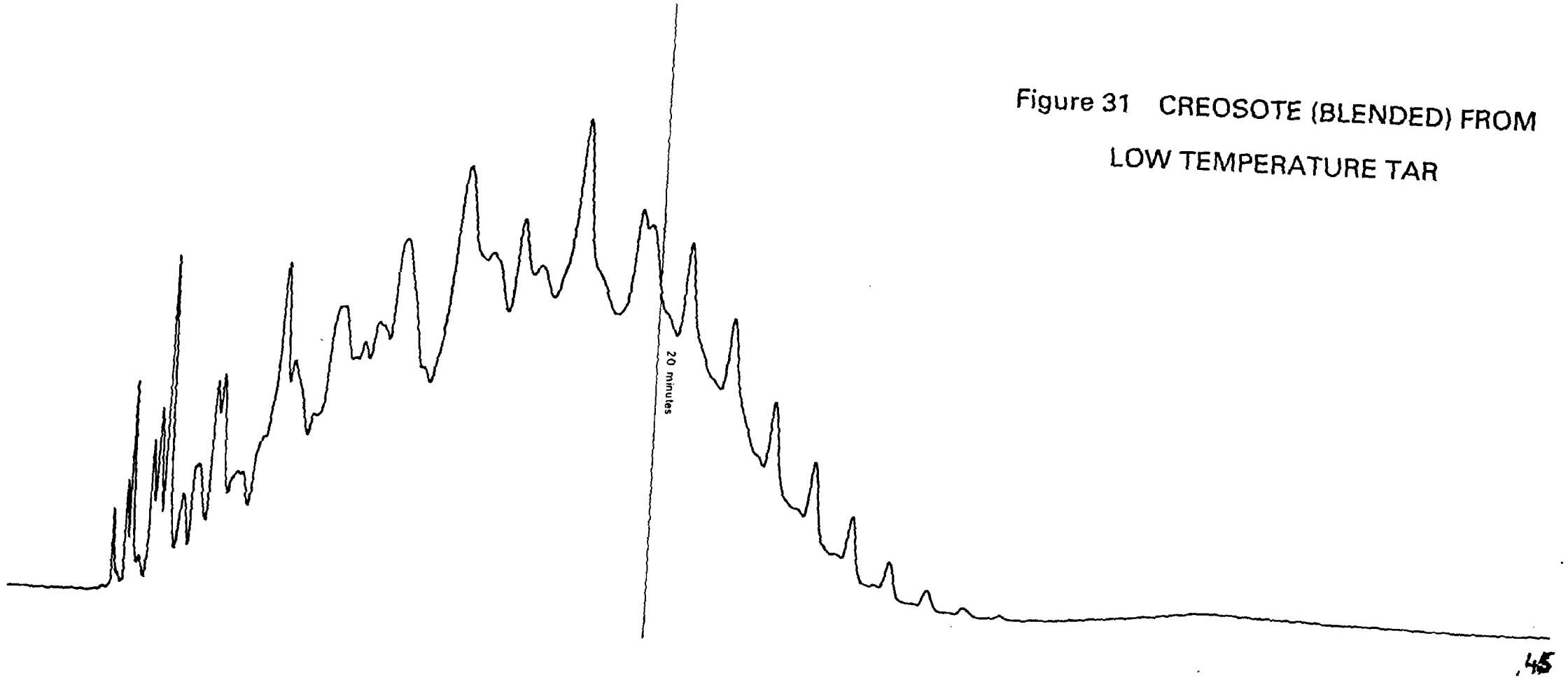
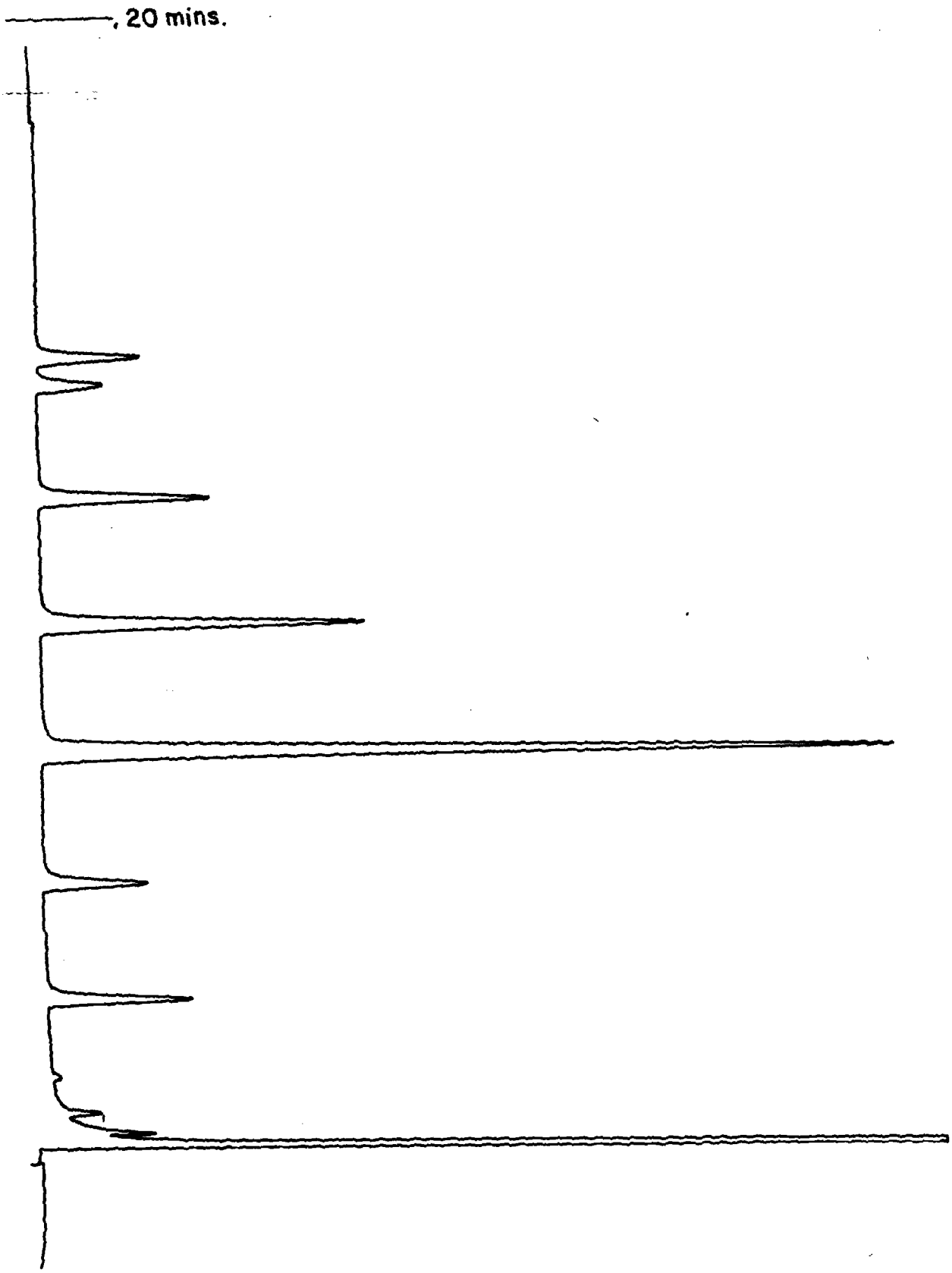


Figure 31 CREOSOTE (BLENDED) FROM LOW TEMPERATURE TAR

Appendix II

Figure 32 COCONUT OIL



Appendix II

Figure 33 RAPESEED OIL

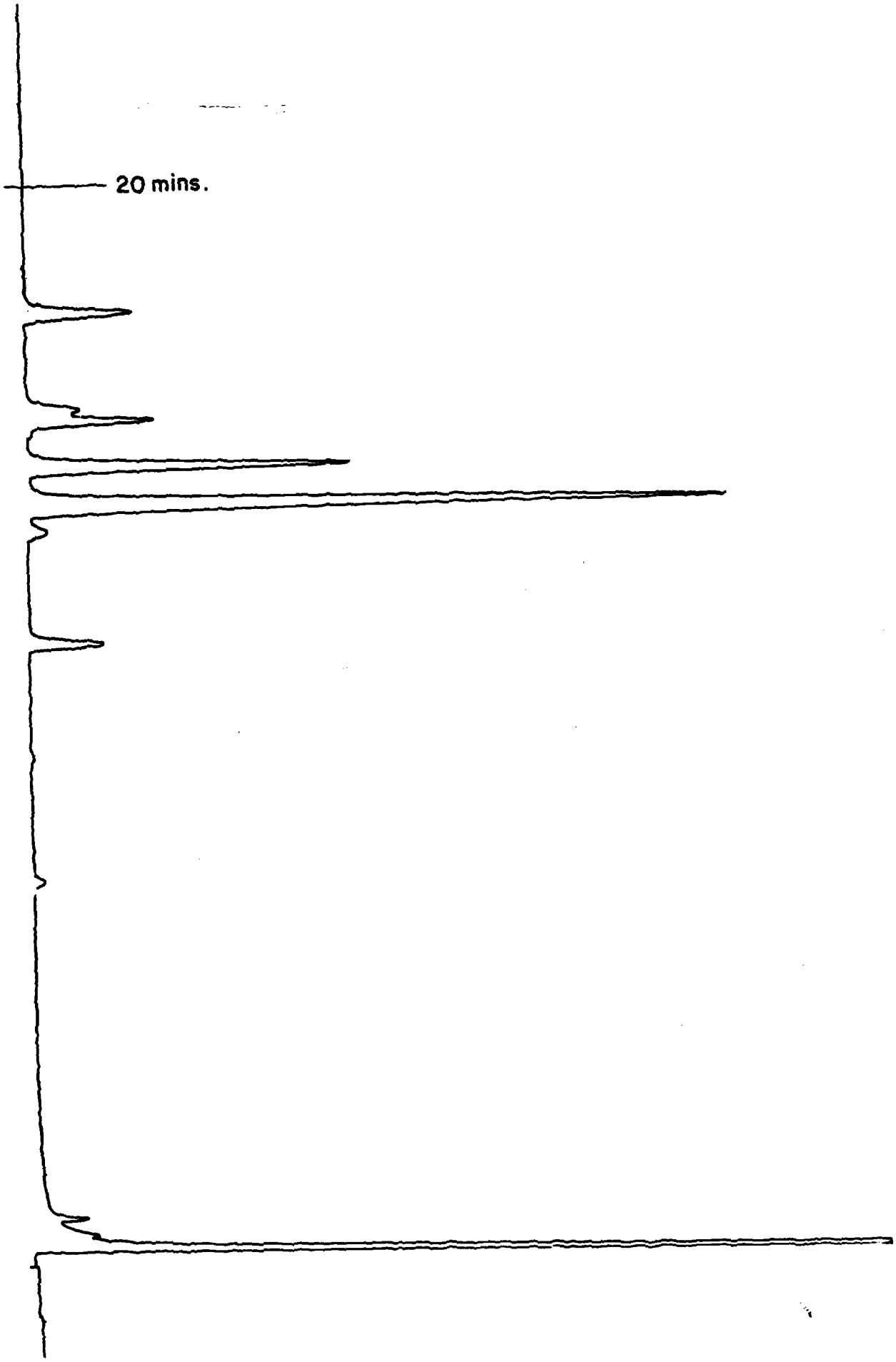
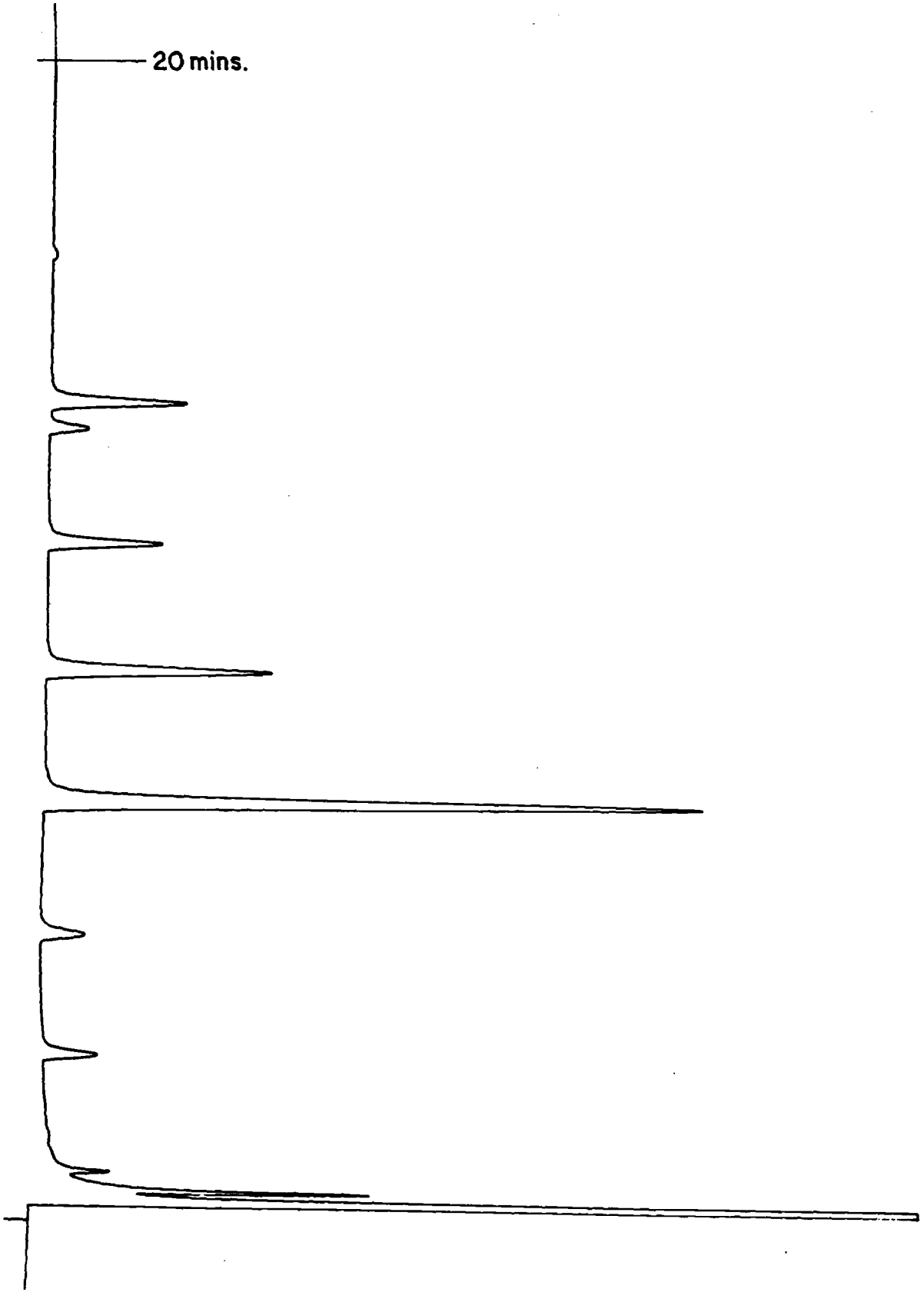
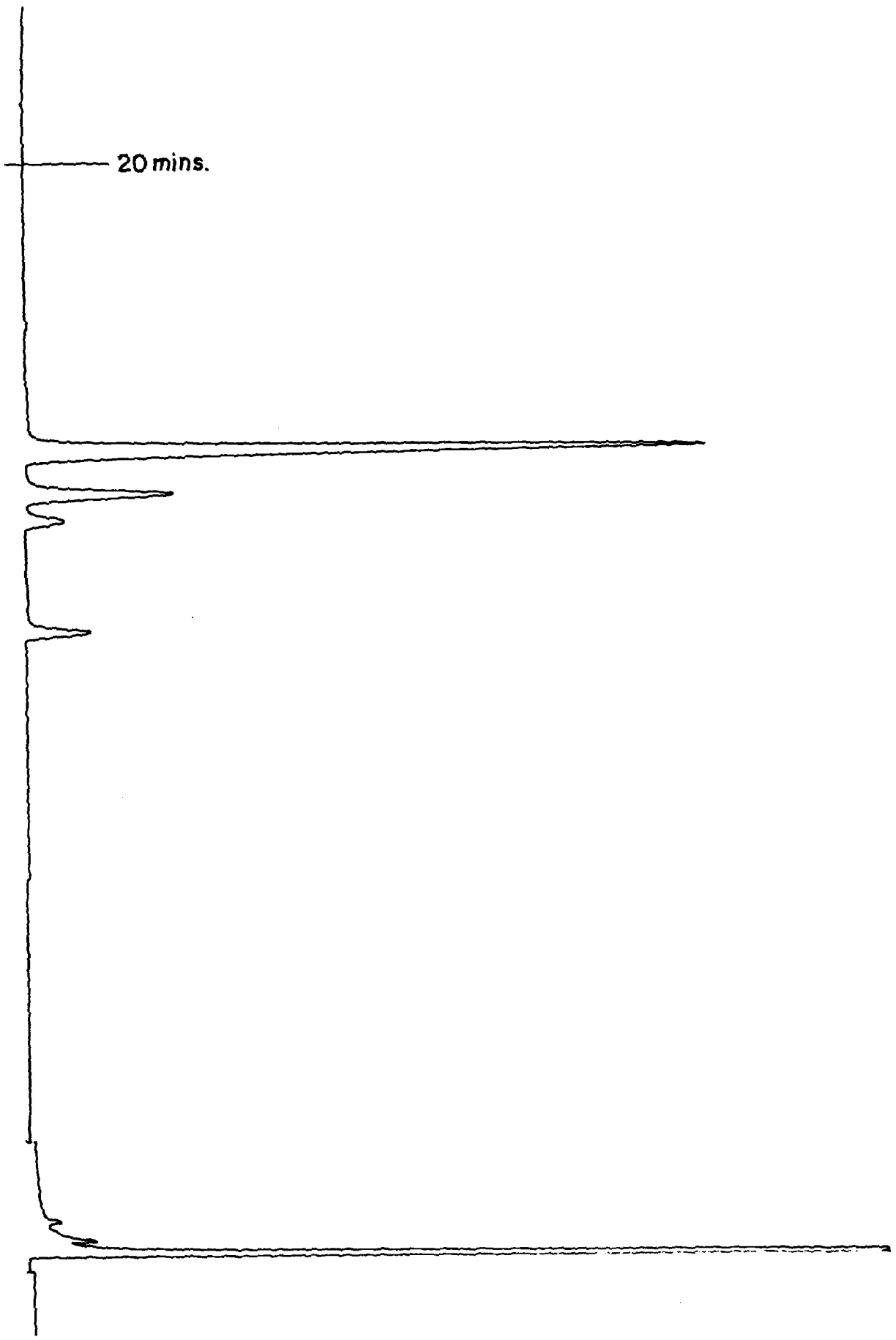


Figure 34 PALM KERNEL OIL



Appendix II

Figure 35 SUNFLOWER



Appendix III

Typical High Resolution Gas Chromatograms for Method D Prepared by Llanelli Area Laboratory, Directorate of Scientific Services Welsh Water Authority

Operating Conditions

Initial temperature	– 100°C
Final temperature	– 220°C
Injector temperature	– 225°C
Detector temperature	– 250°C
Programme rate	– 4°C min^{-1}
Chart speed	– 1 cm min^{-1}
Column	– 50 metre glass open tube capillary wall coated with OV101
Gas	– Nitrogen at 2 ml min^{-1}
Splitter ratio	– 20:1
Gas Chromatograph	– VARIAN 2700
Recorder	– VARIAN 9176 (0- 1mV full scale deflection)

Reference Chromatograms in Appendix III

	See Notes	Respective Figures
North Sea Crude Oil (Beatrice)	a,b,c,	39, 37, 44
Kuwait Crude Oil	a,b,c	45, 50, 41
Medium Fuel Oil	a,b,c	42, 52, 47
Heavy Fuel Oil	a,b,c	61, 59, 49
White Spirit		48
Gas Oil	b,c	53, 55
Non soluble cutting oil	a,b,c	36, 54, 38
Creosote blended (from high and low temperature tars)	a,b,c	40, 58, 57
Cresote blended (from low temperature tars)	a,b,c	60, 56, 46
Low temperature tar	a,c	51,43

Notes

The Chromatograms indicated are given in Appendix III
a – Distillate
b – 10% distillate in pentane solution
c – 10% pentane extract cleaned up with Florisil.

Figure 36 NON-SOLUBLE CUTTING OIL

a) Distillate

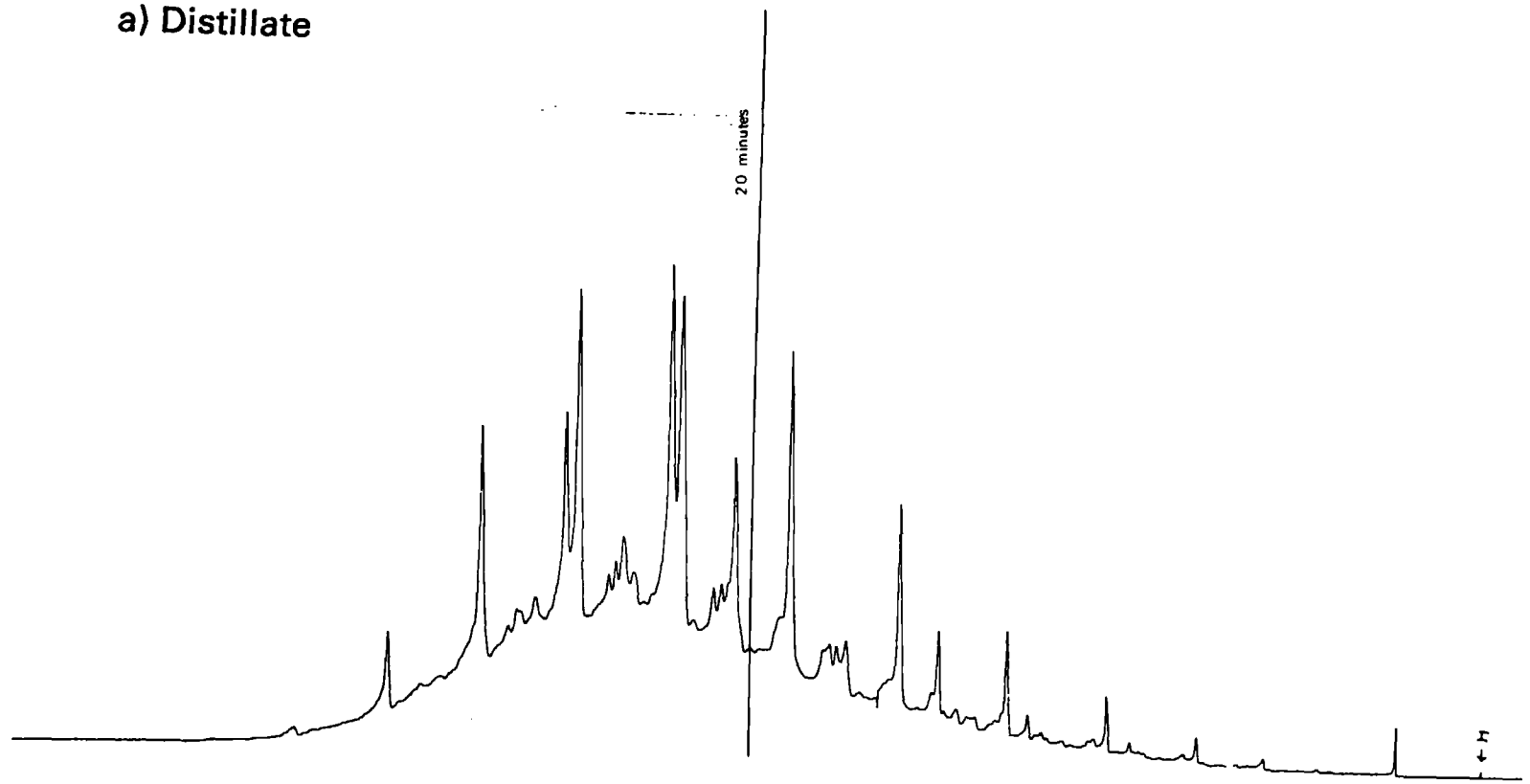


Figure 38 NON-SOLUBLE CUTTING OIL

c) Pentane extract (10%) (cleaned up with Florisil)

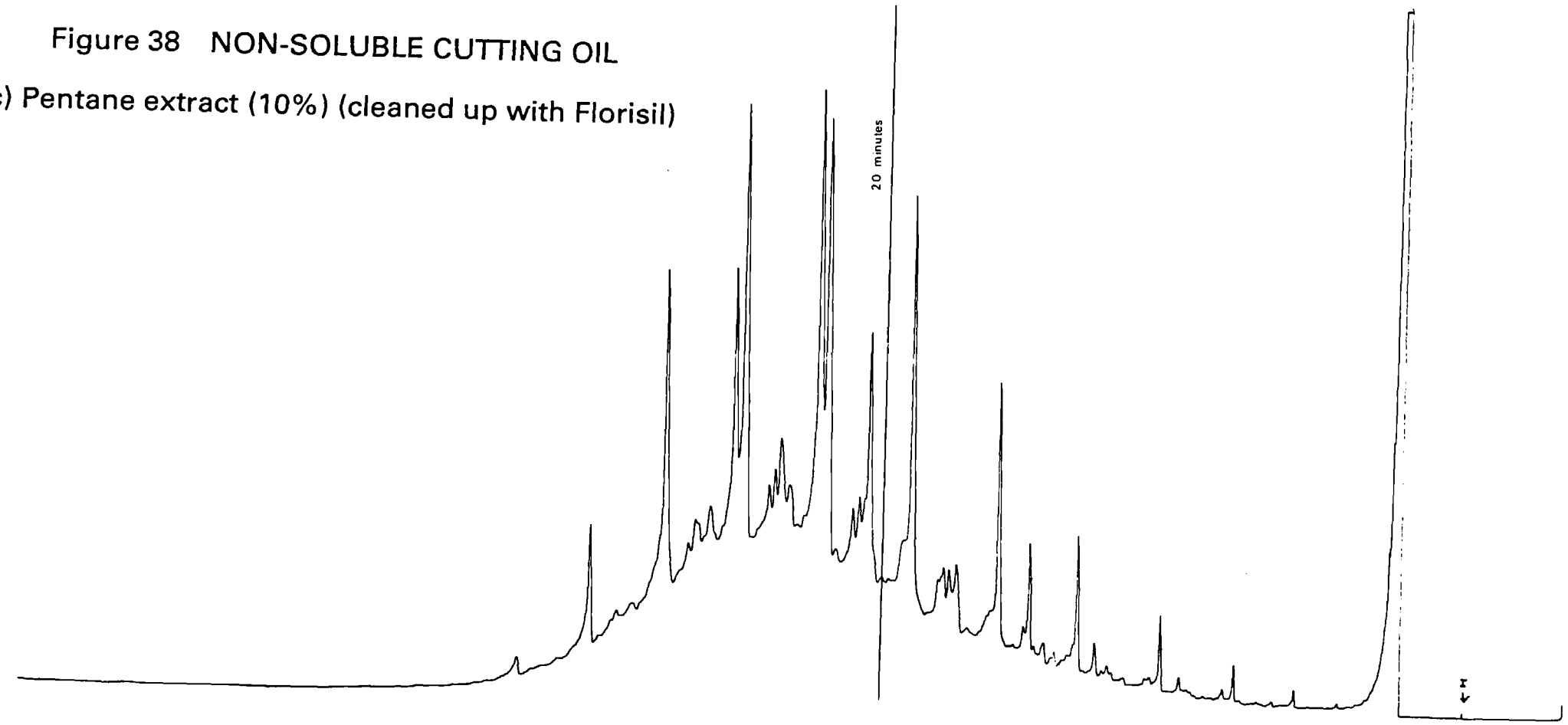


Figure 37 NORTH SEA CRUDE OIL (BEATRICE)

b) 10% Distillate in Pentane

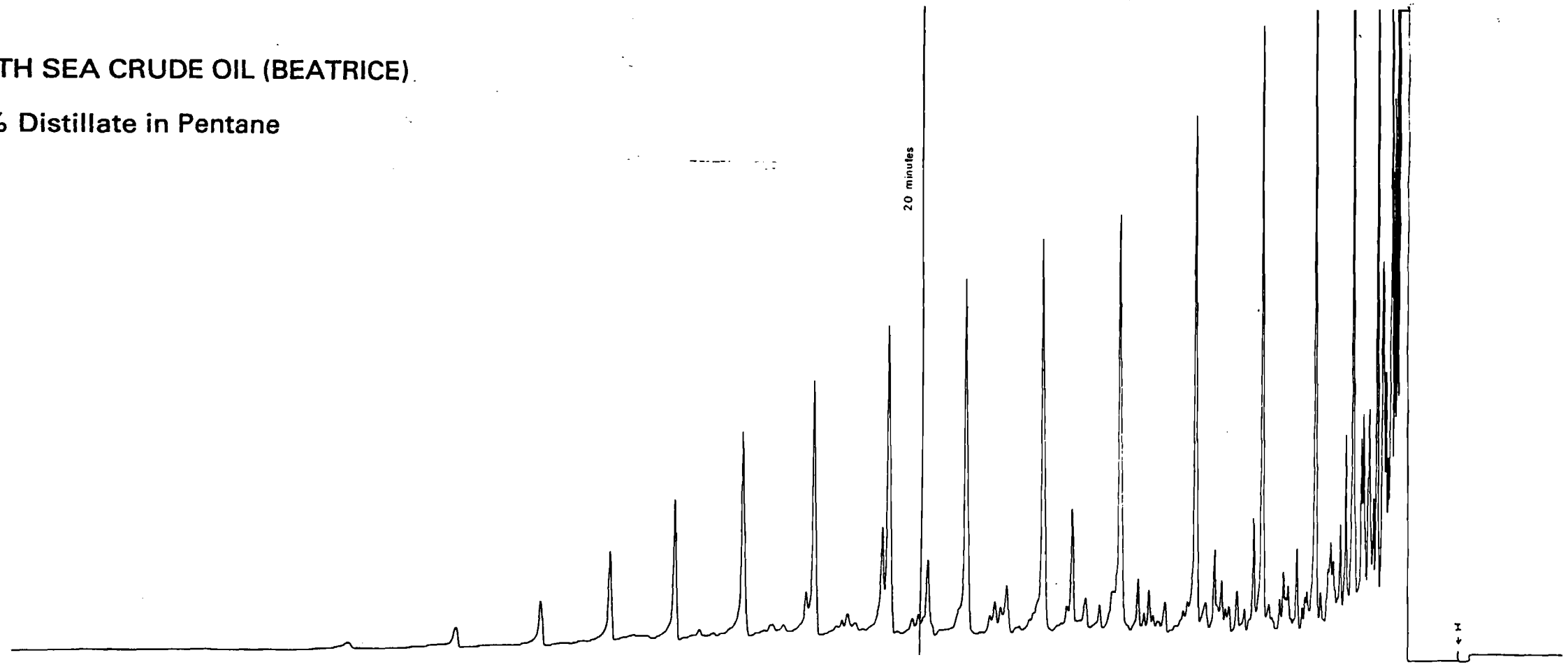


Figure 39 NORTH SEA CRUDE OIL (BEATRICE)

a) Distillate

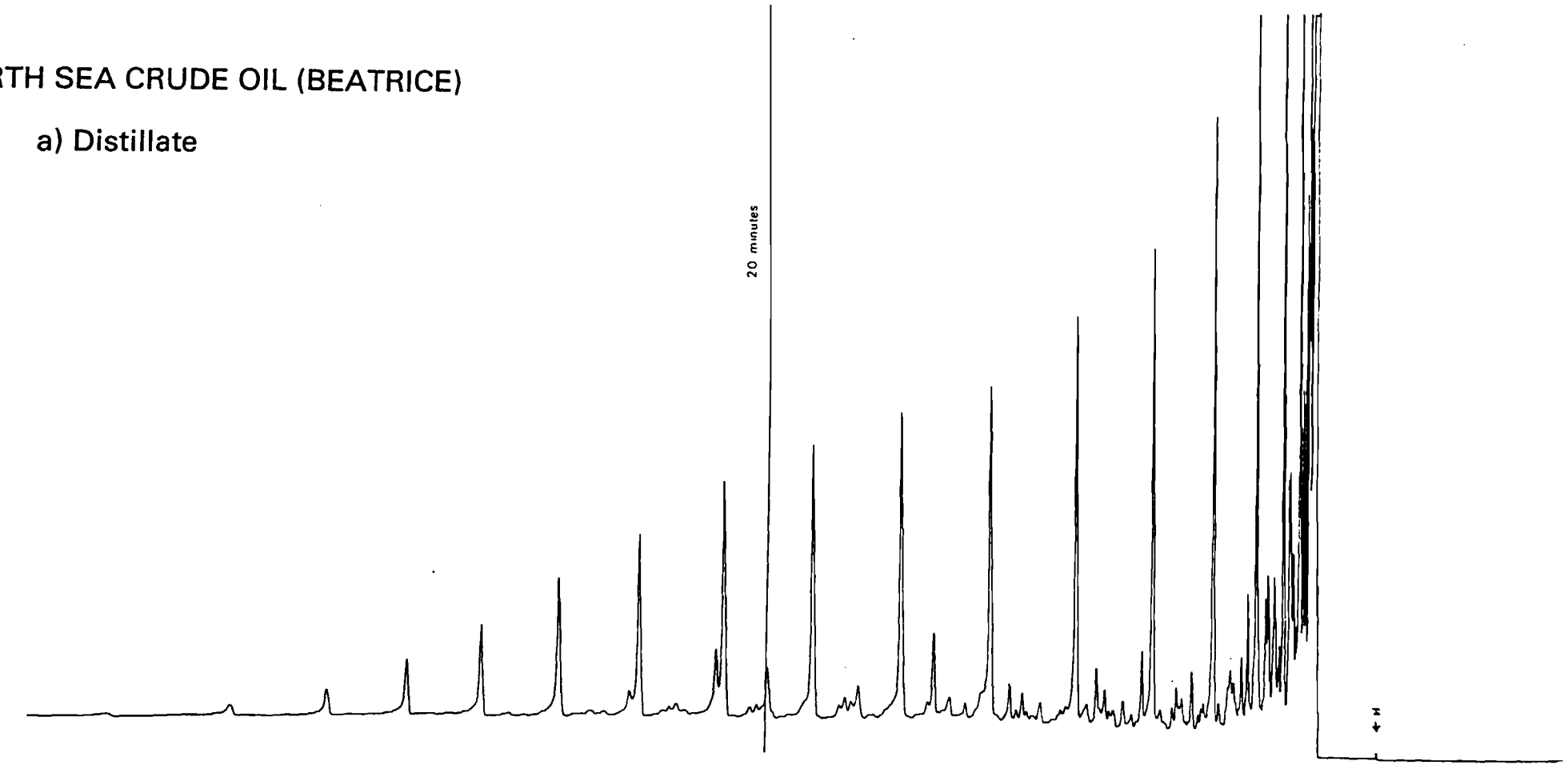


Figure 40 CREOSOTE BLENDED FROM HIGH AND LOW TEMPERATURE TARS

a) Distillate

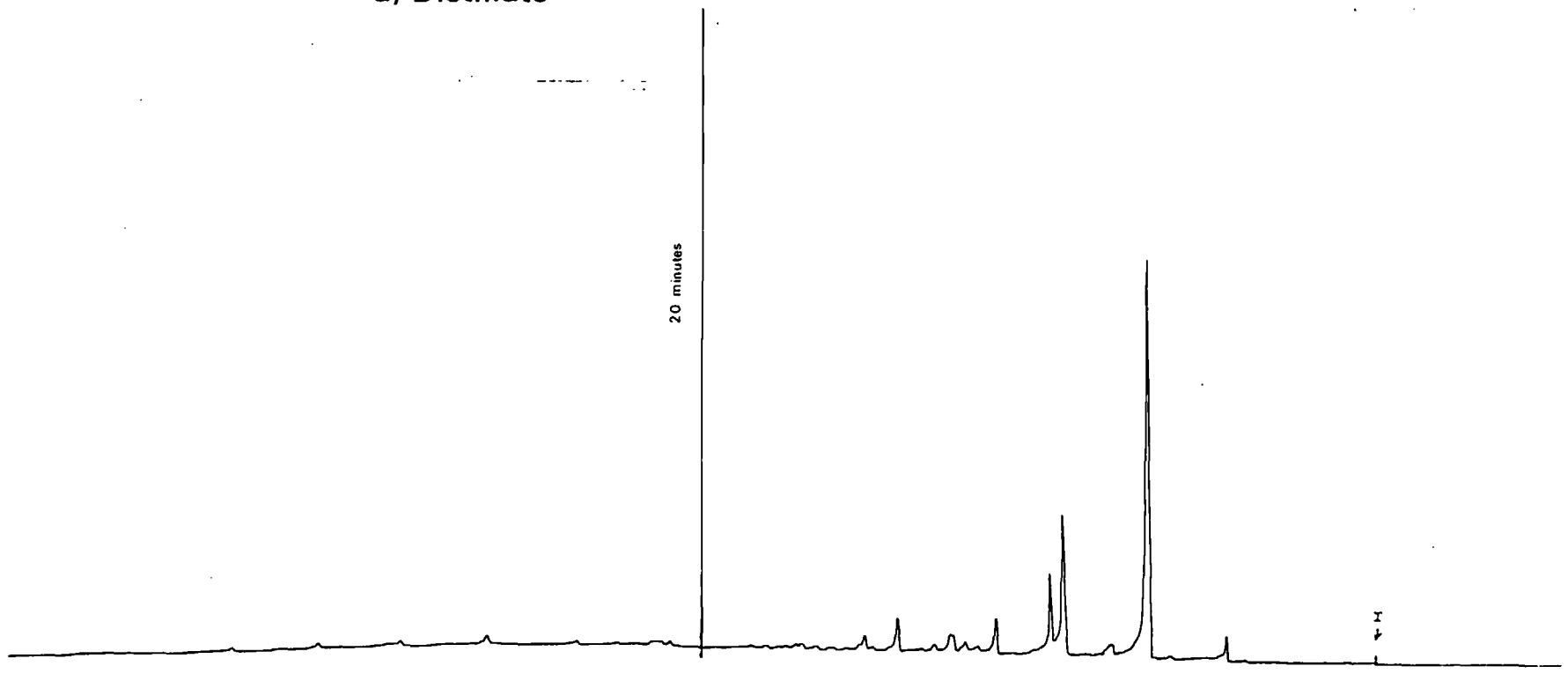


Figure 42 MEDIUM FUEL OIL

a) Distillate

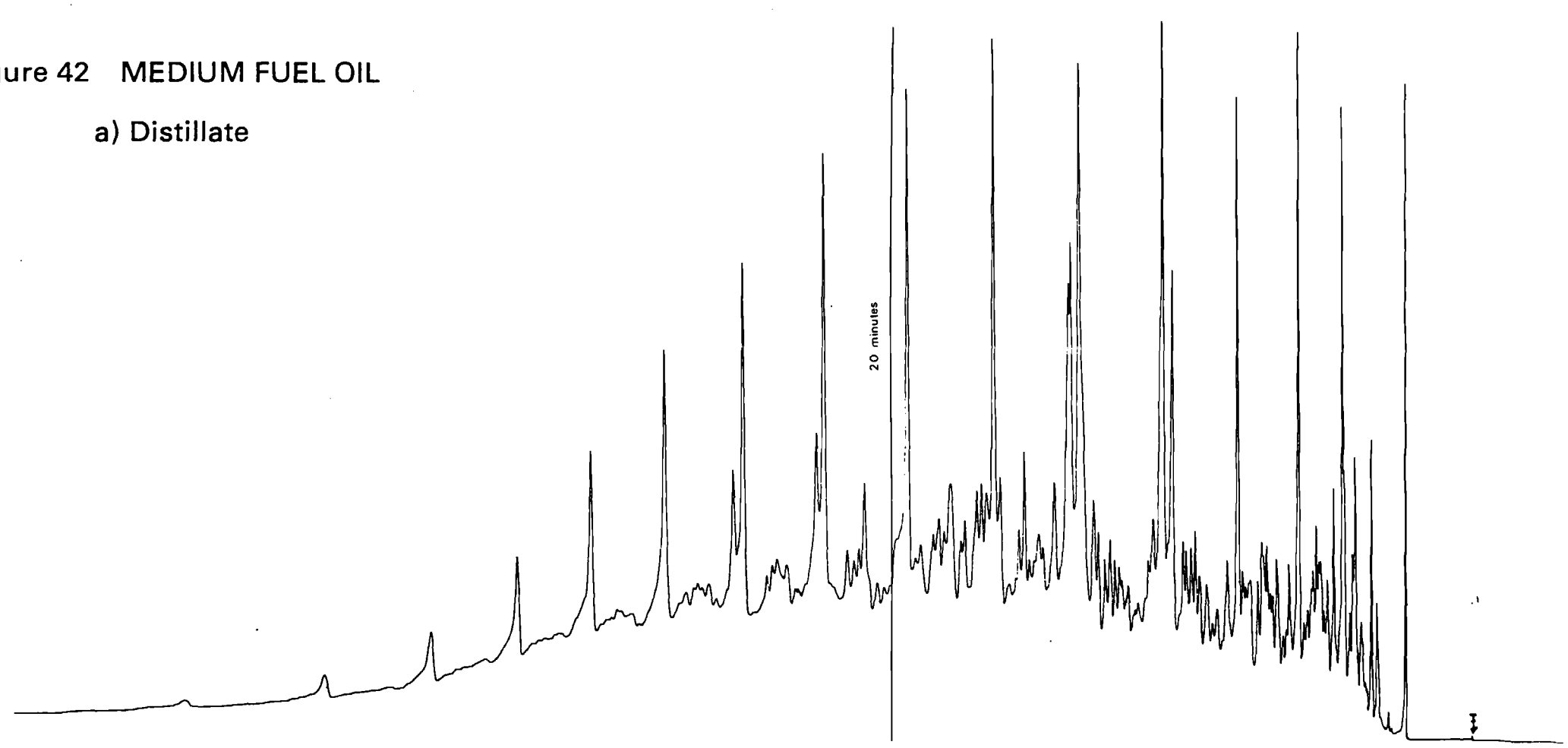


Figure 41 KUWAIT CRUDE OIL

c) Pentane extract (10%) (cleaned up with Florisil)

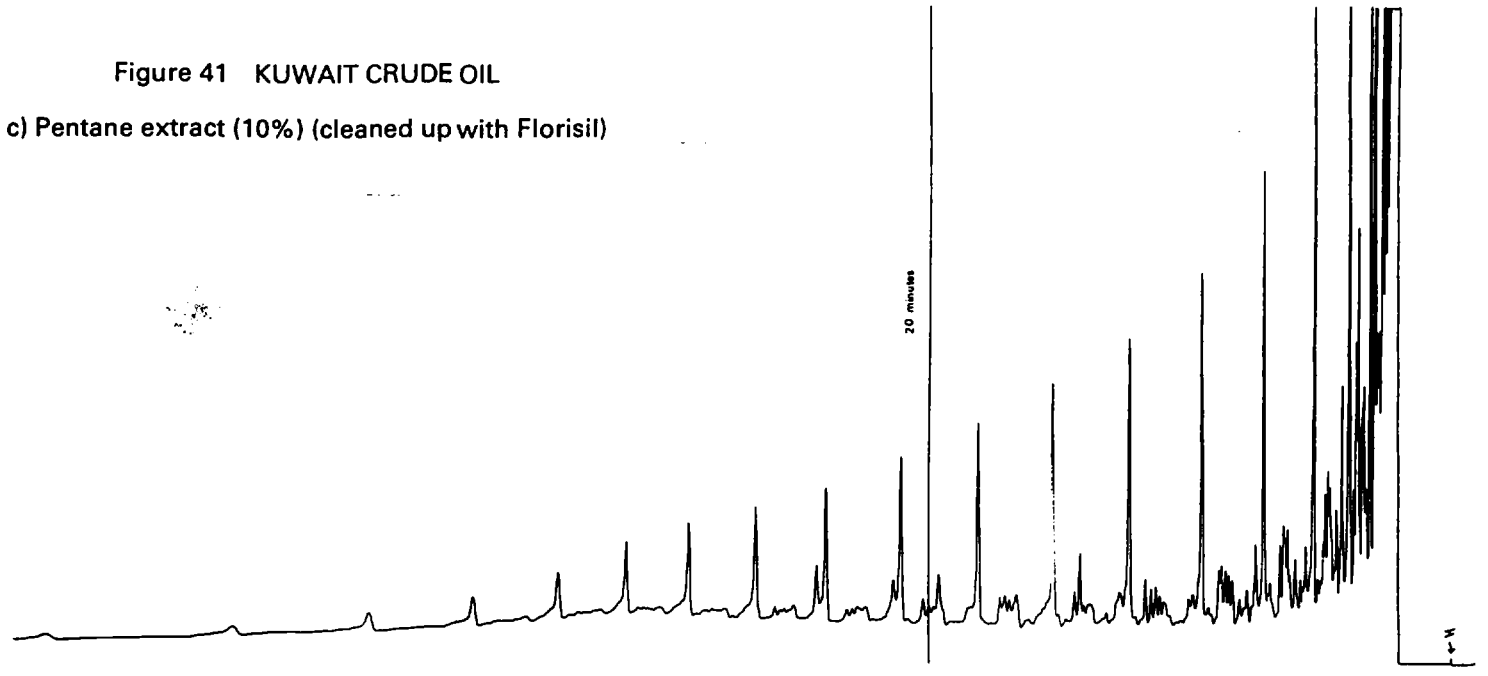


Figure 43 LOW TEMPERATURE TAR

c) Pentane extract (10%) (cleaned up with Florisil)

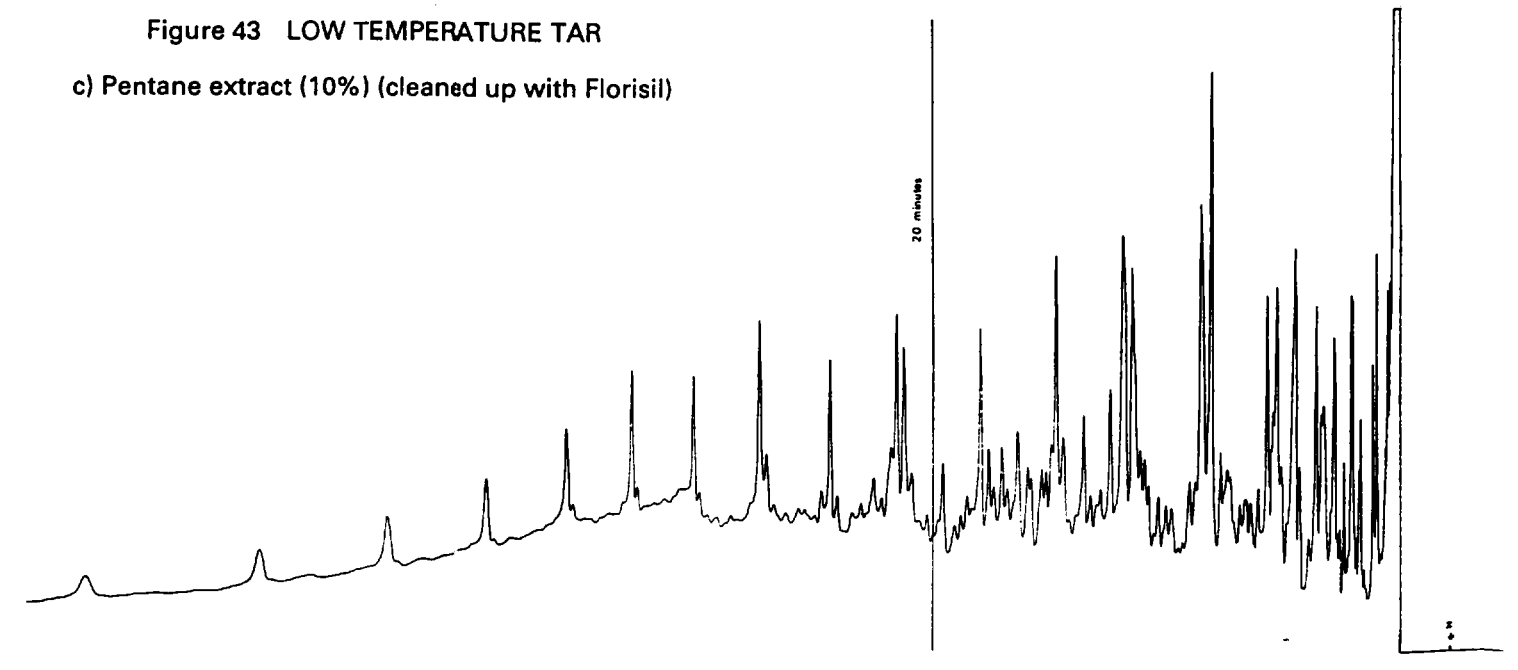


Figure 44 NORTH SEA CRUDE OIL (BEATRICE)

c) Pentane extract (10%) (cleaned up with Florisil)

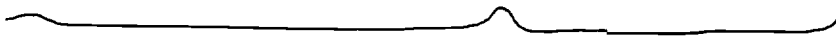


Figure 45 KUWAIT CRUDE OIL

a) Distillate

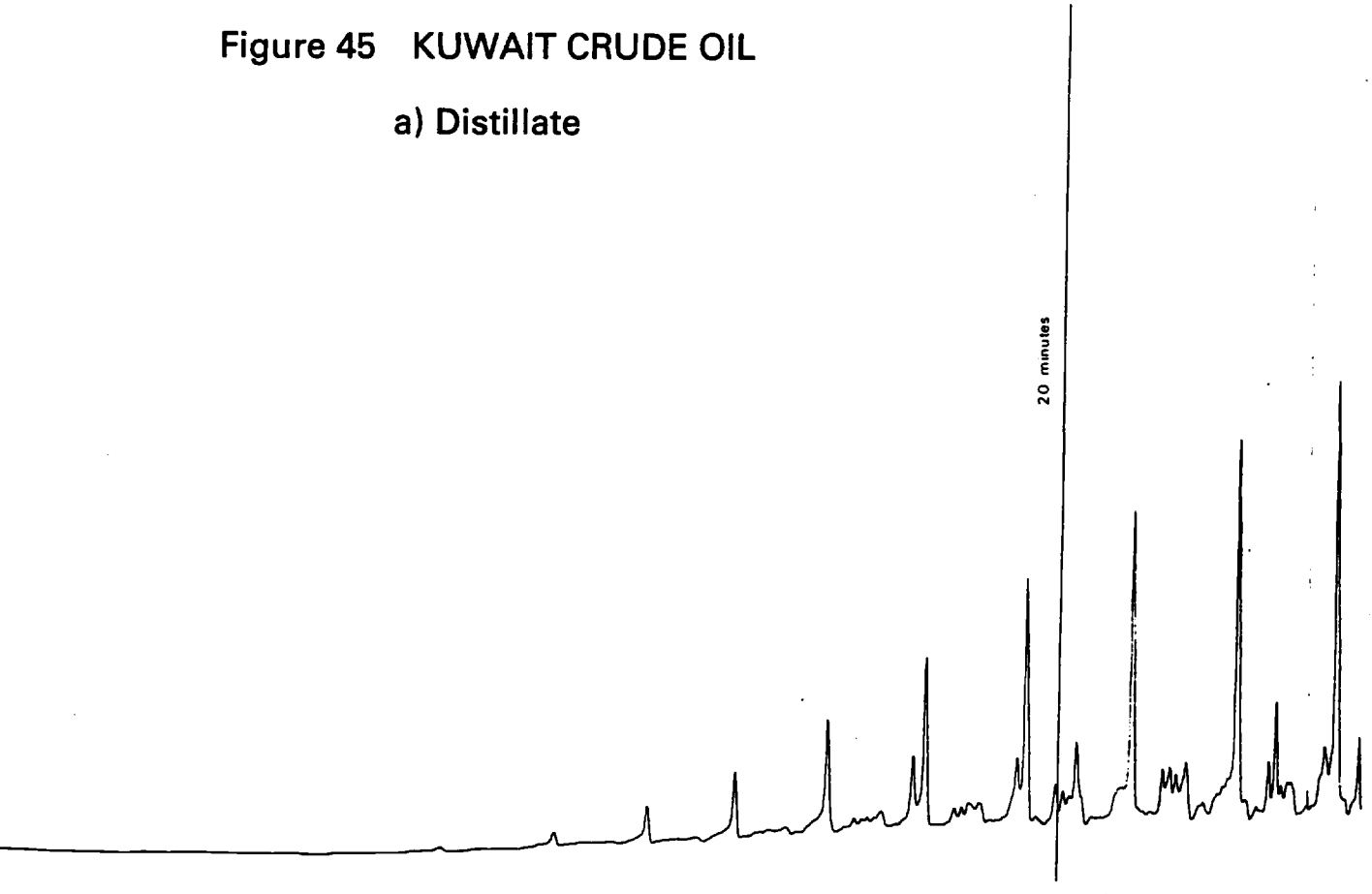


Figure 44 (cont.)

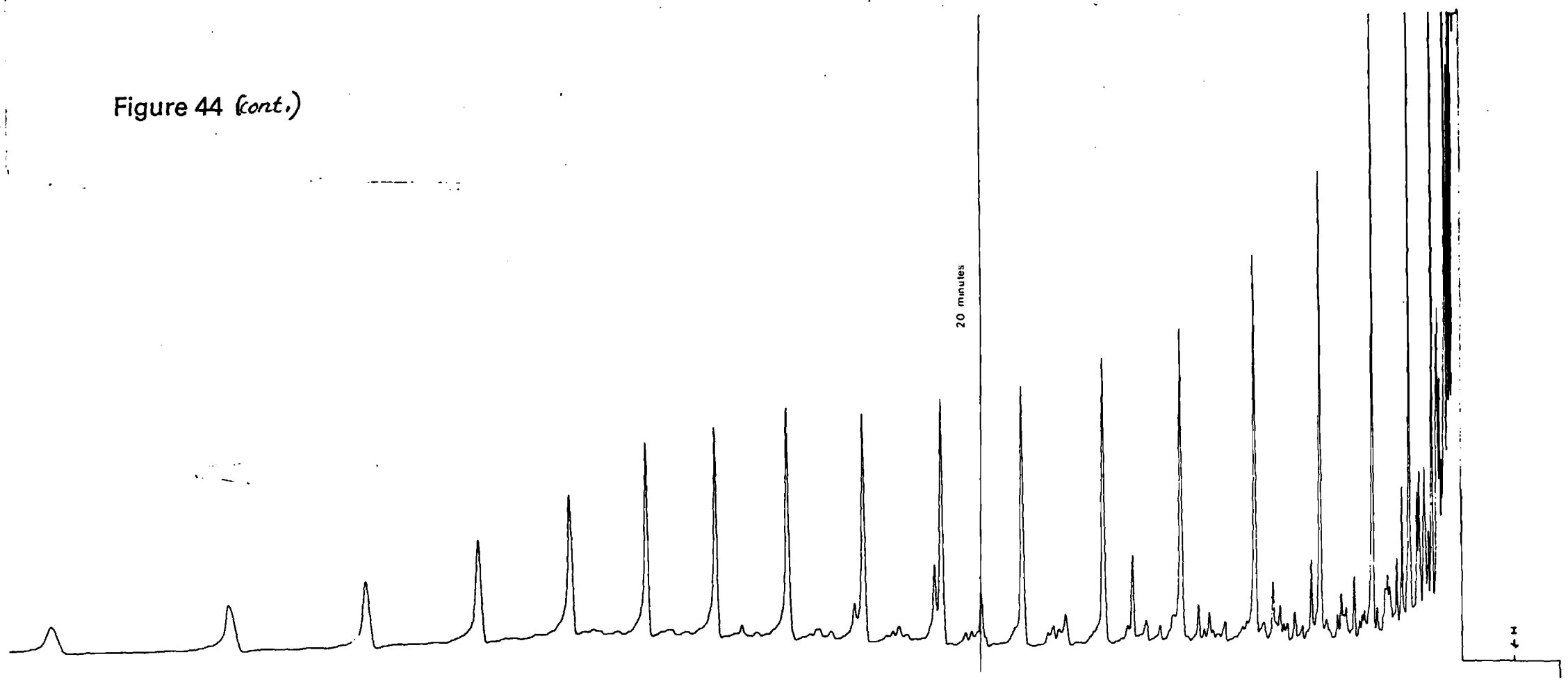


Figure 45 (cont.)

Figure 46 CREOSOTE BLENDED FROM LOW TEMPERATURE TAR

c) Pentane extract (10%) (cleaned up with Florisil)

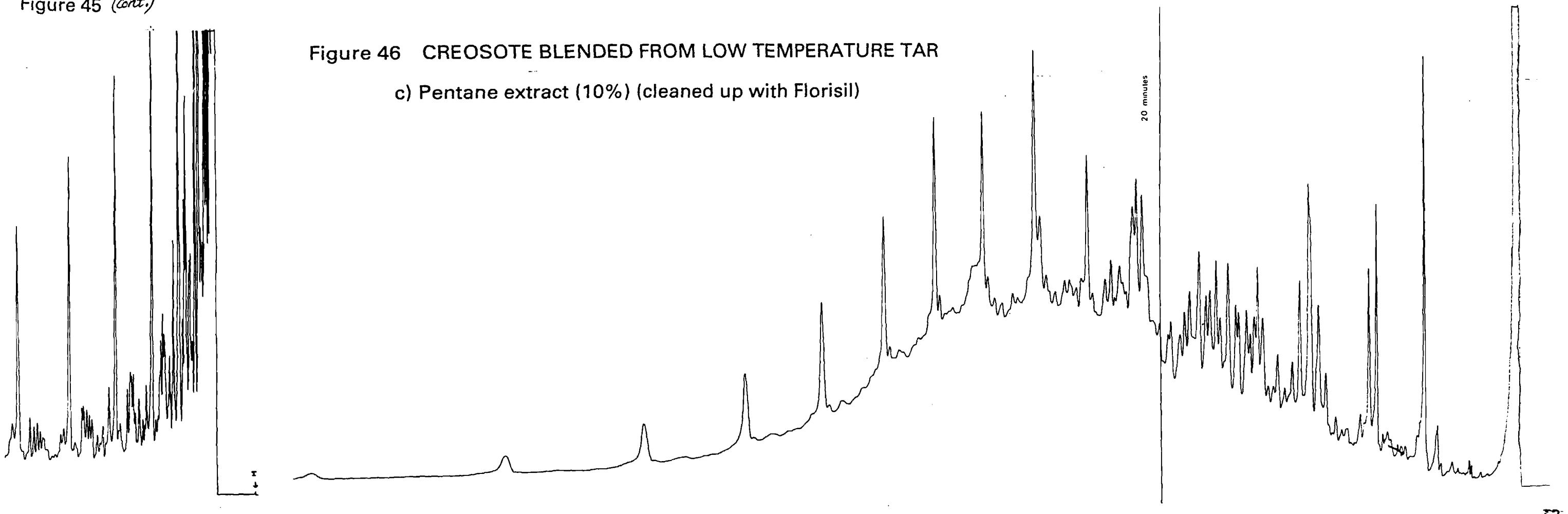


Figure 47 MEDIUM FUEL OIL

c) Pentane extract (10%) (cleaned up with Florisil)

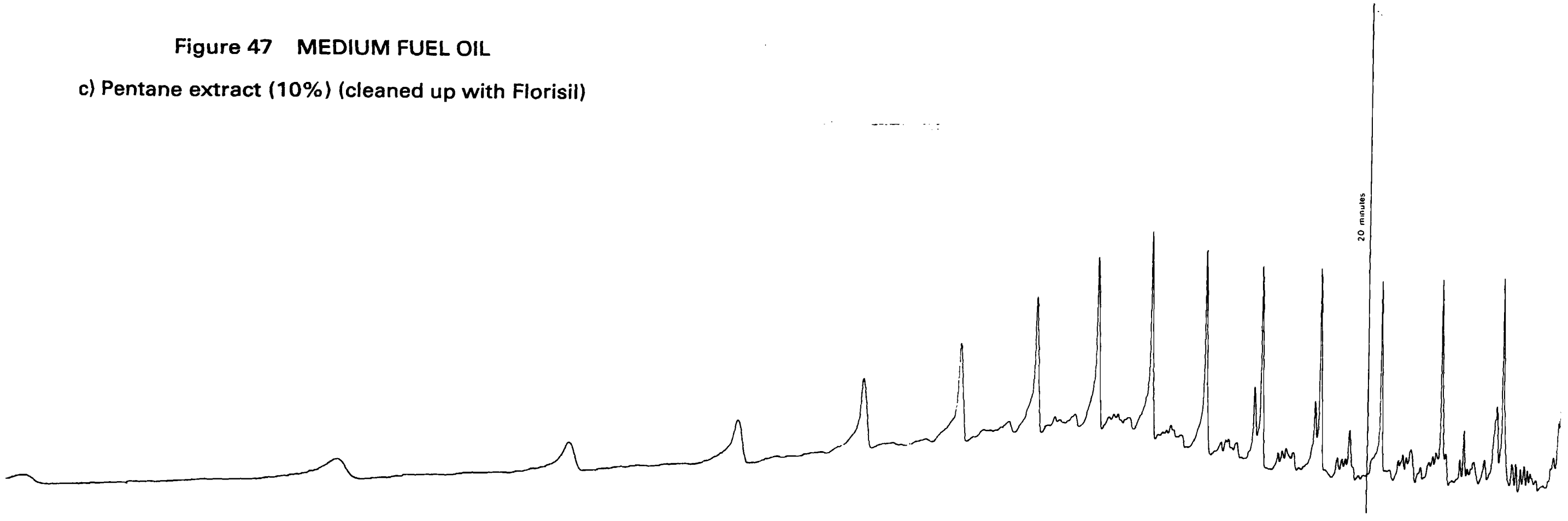


Figure 49 HEAVY FUEL OIL

c) Pentane extract (10%) (cleaned up with Florisil)

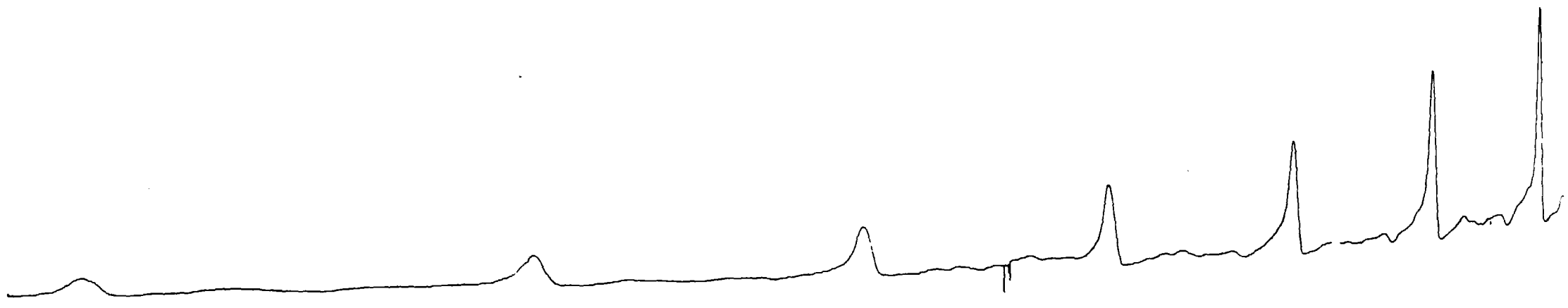


Figure 47 *(cont.)*

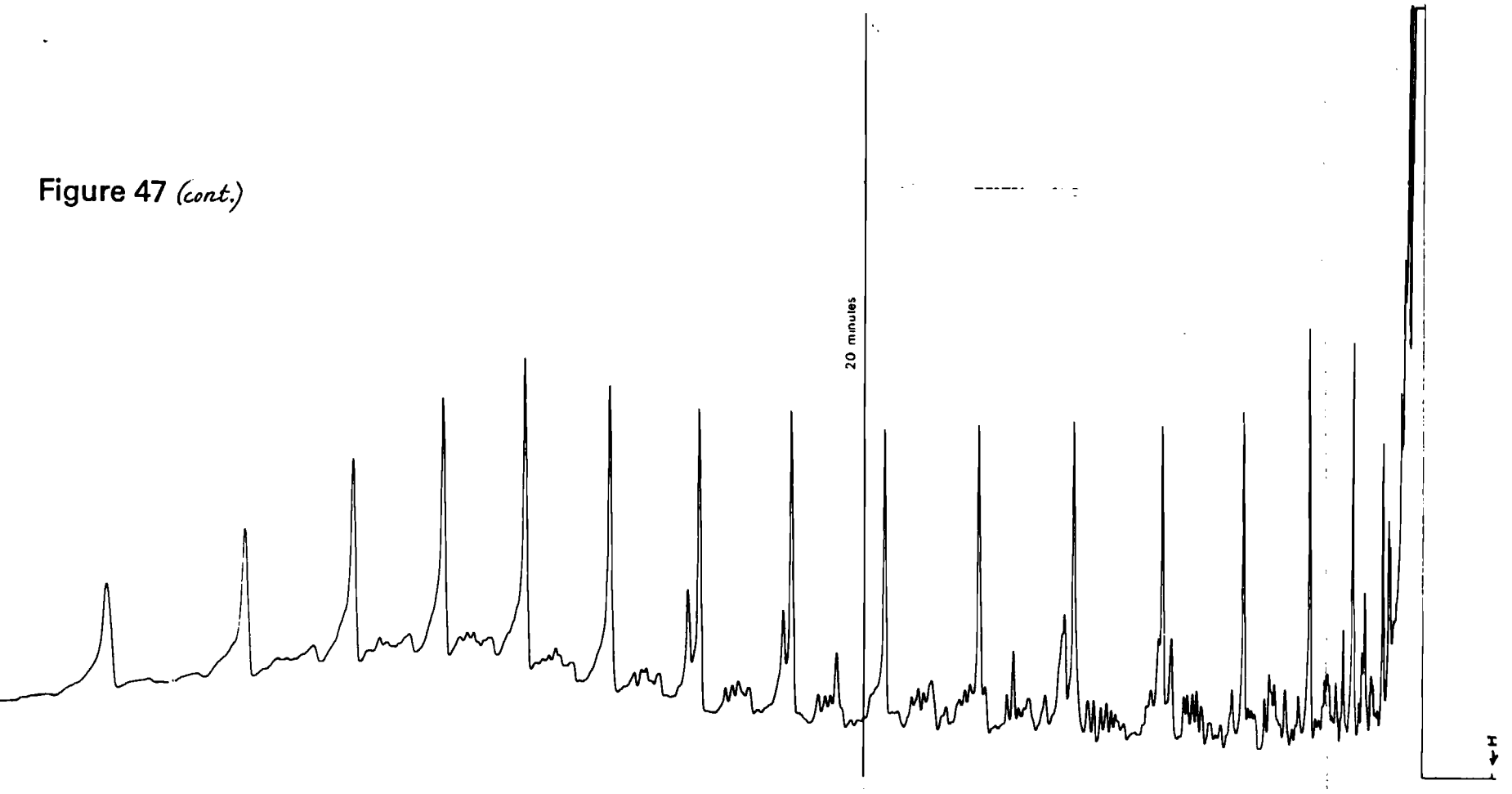


Figure 48 WHITE SPIRIT

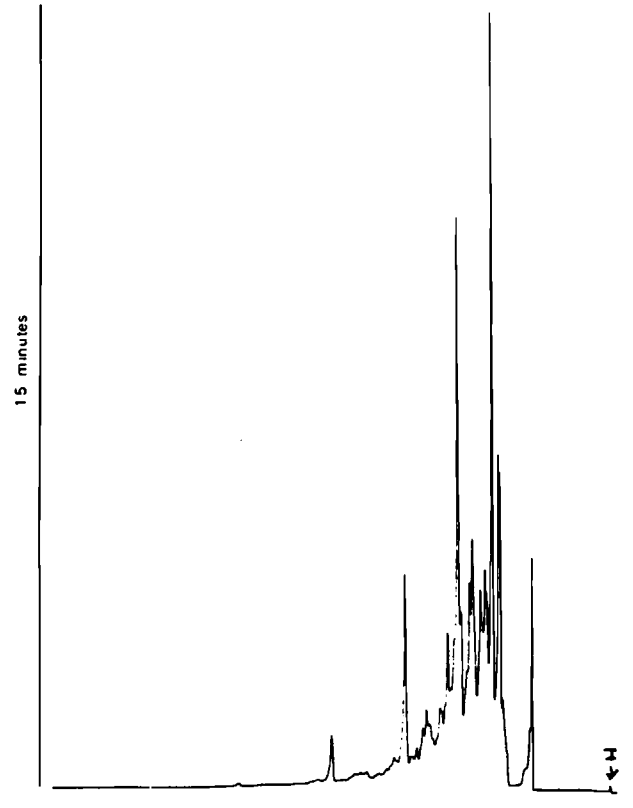


Figure 49 *(cont.)*

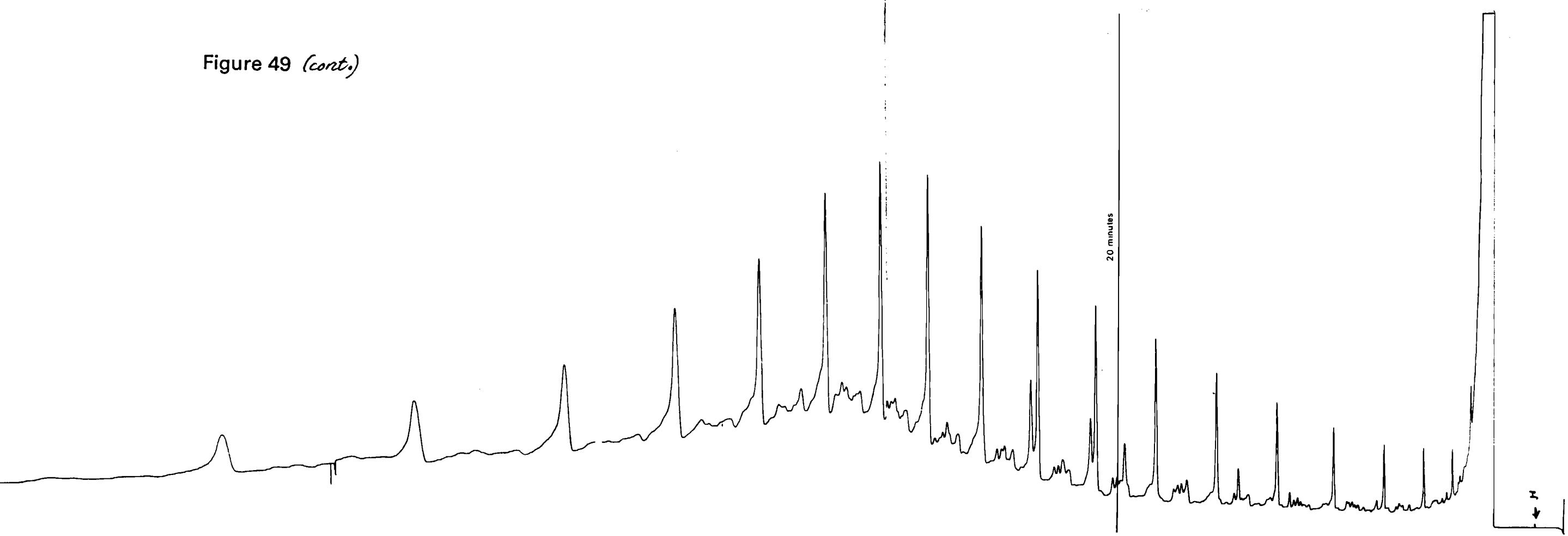


Figure 50 LOW TEMPERATURE TAR

a) Distillate

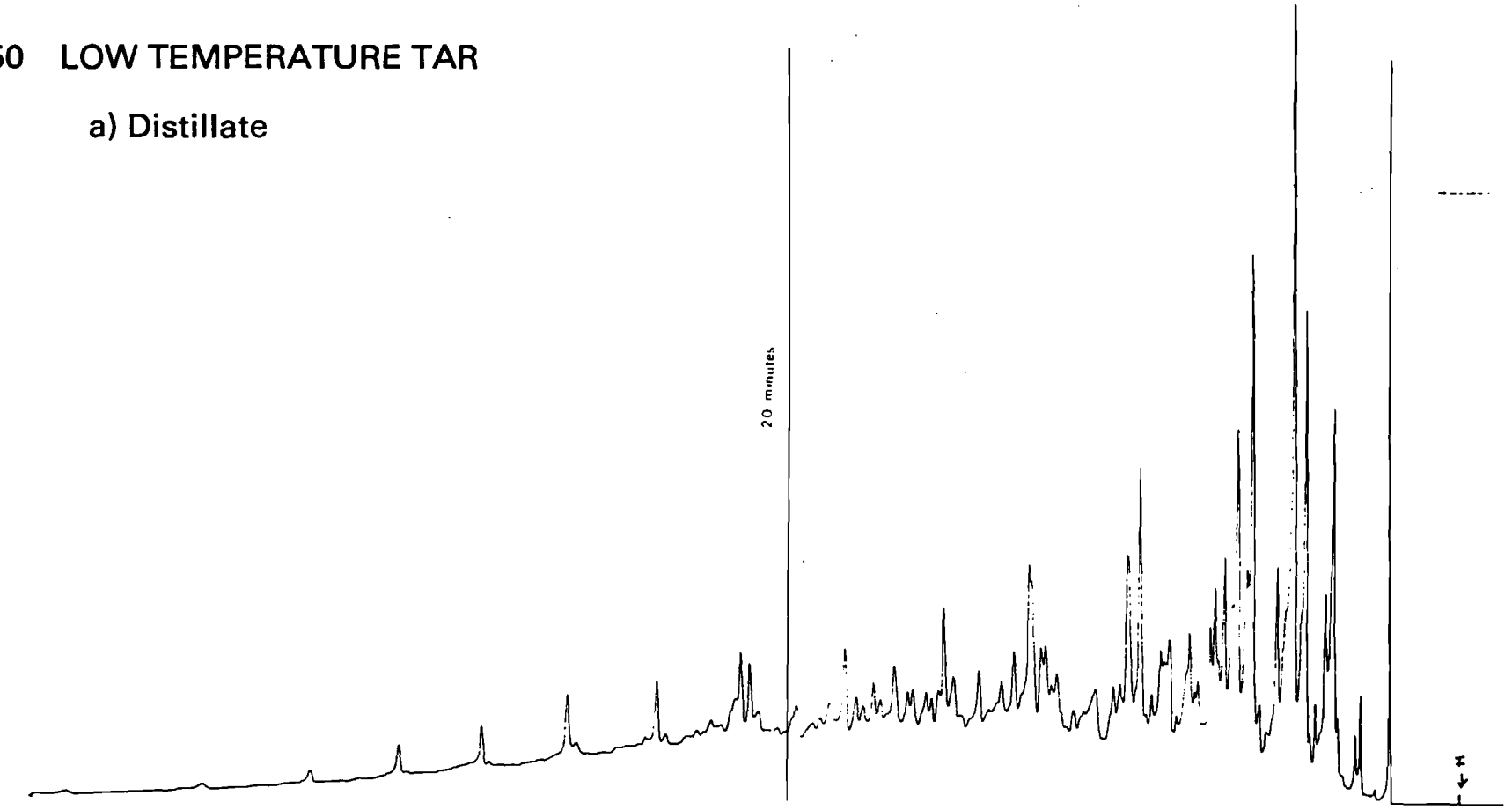


Figure 52 MEDIUM FUEL OIL

b) 10% Distillate in Pentane

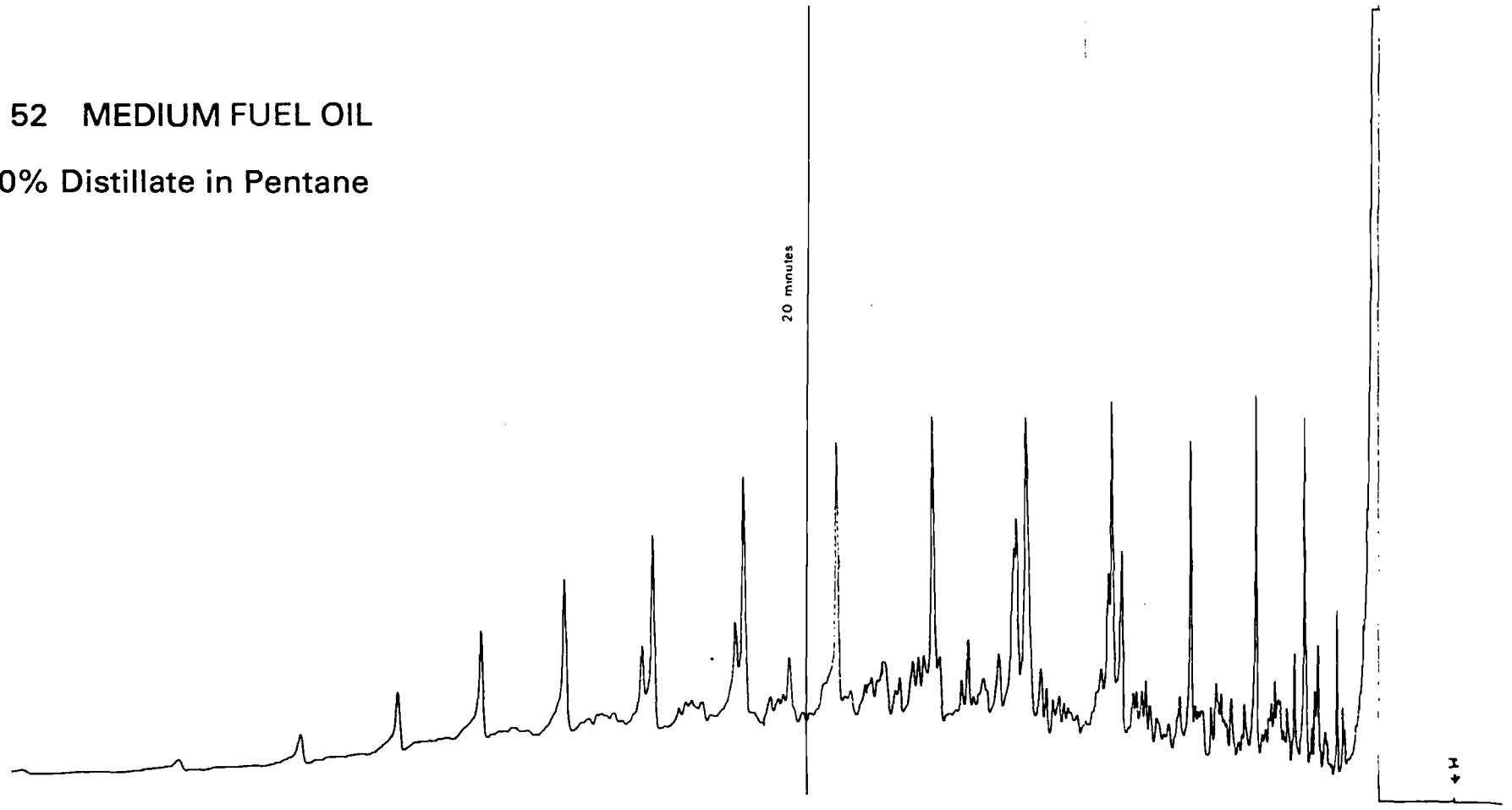


Figure 51 KUWAIT CRUDE OIL

b) 10% Distillate in Pentane

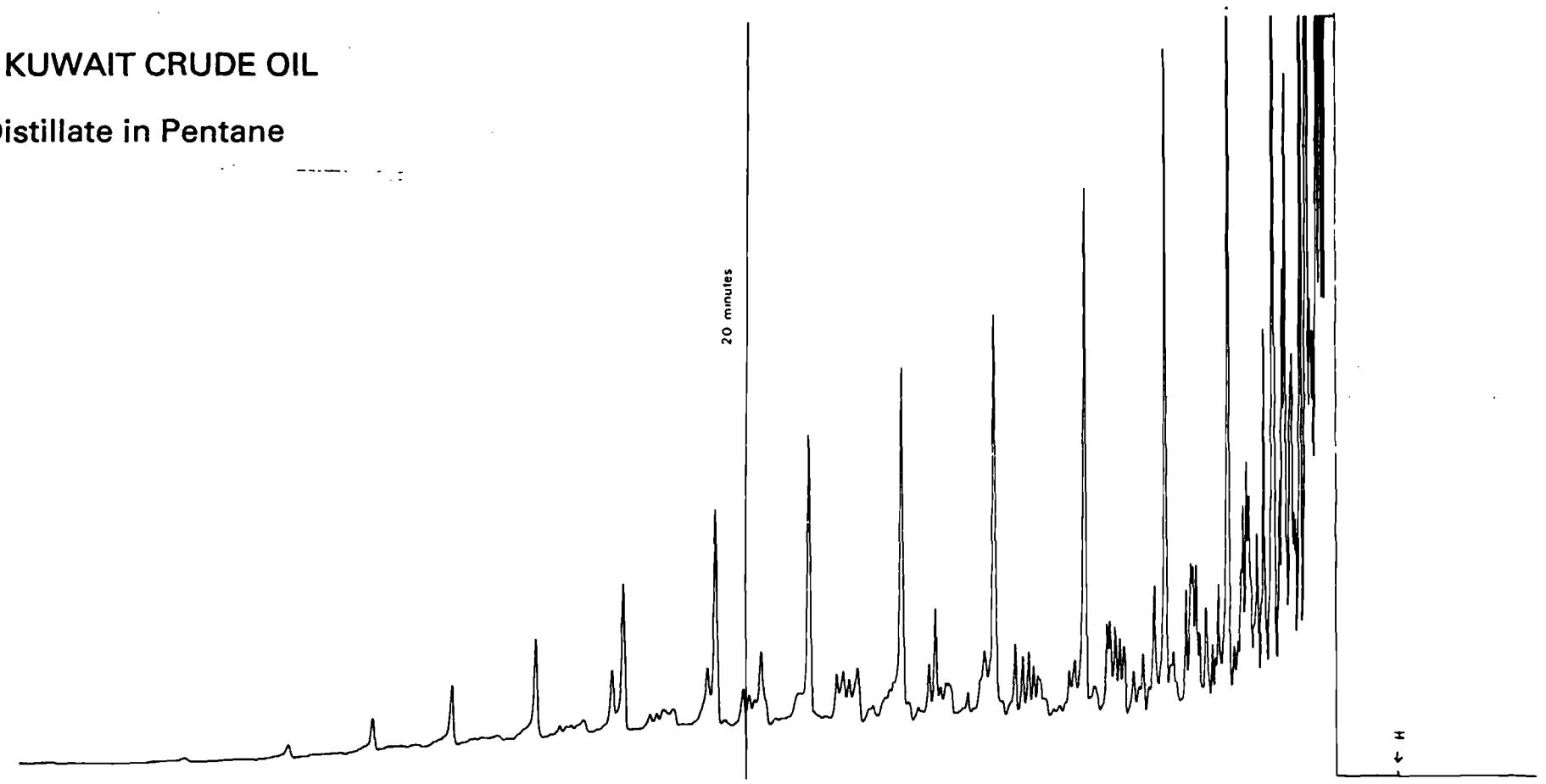


Figure 53 GAS OIL

b) 10% Distillate in Pentane

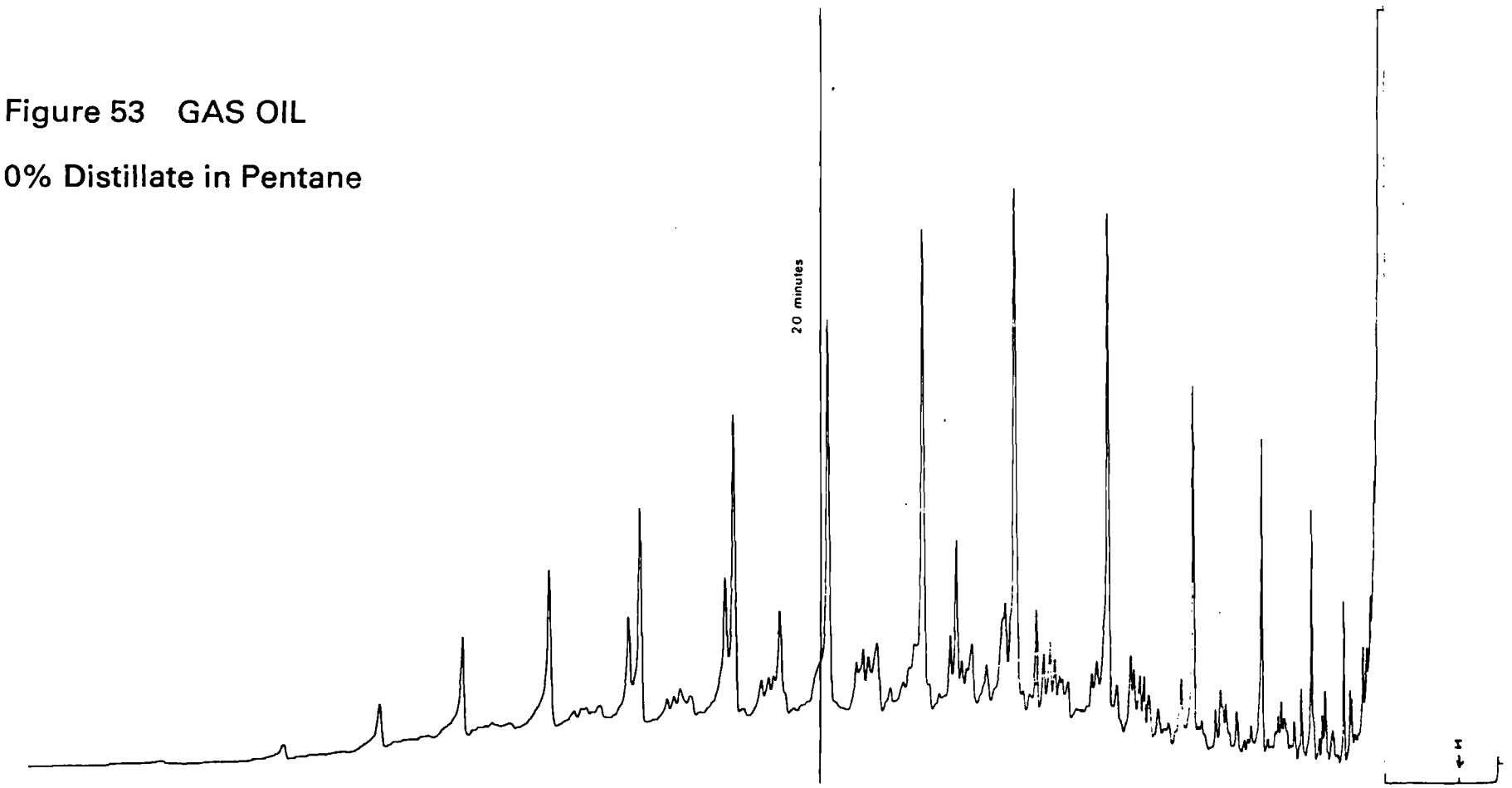


Figure 54 NON-SOLUBLE CUTTING OIL

b) 10% Distillate in Pentane

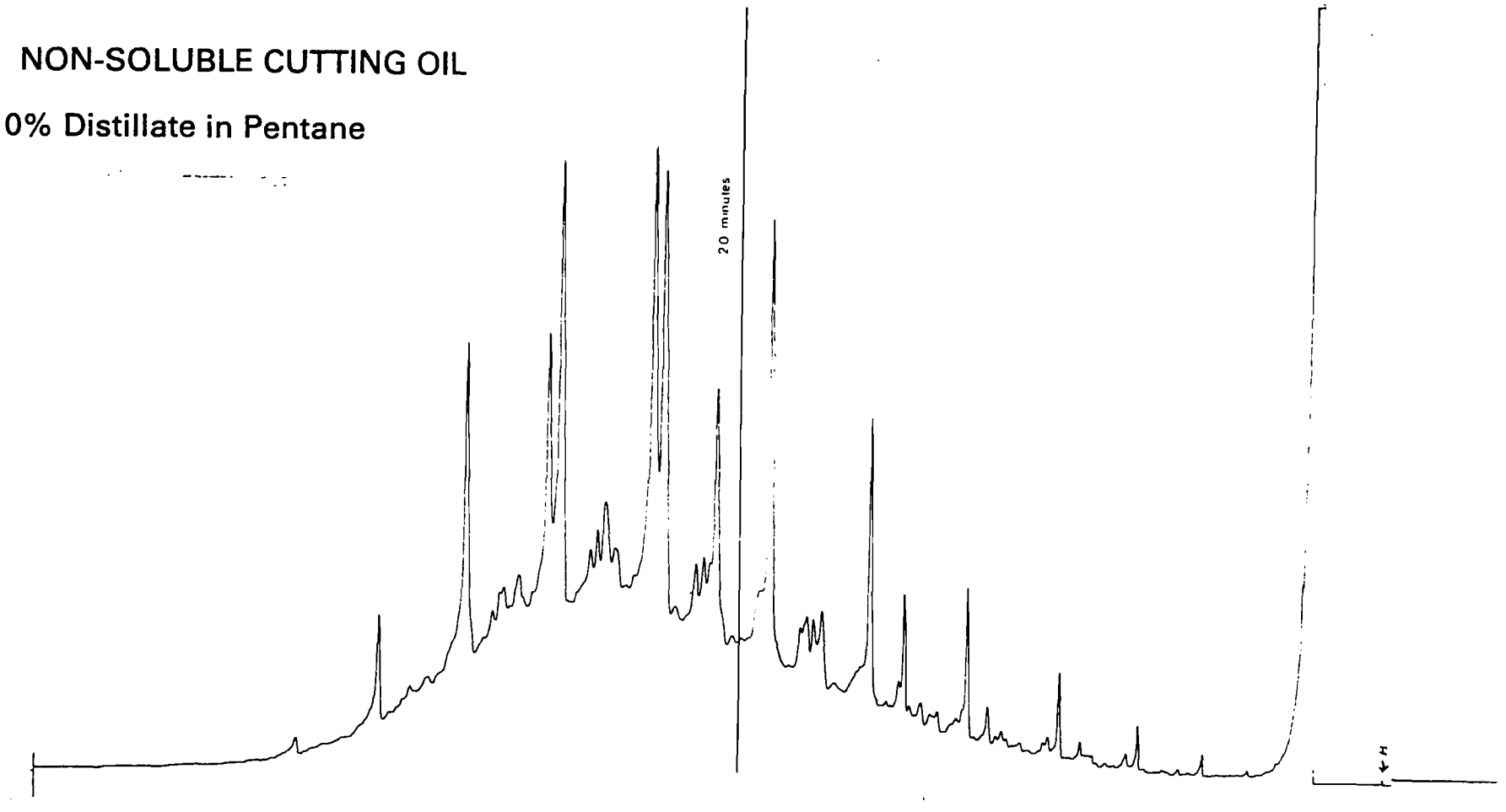


Figure 56 CREOSOTE BLENDED FROM LOW TEMPERATURE TAR

b) 10% Distillate in Pentane (cleaned up with Florisil)

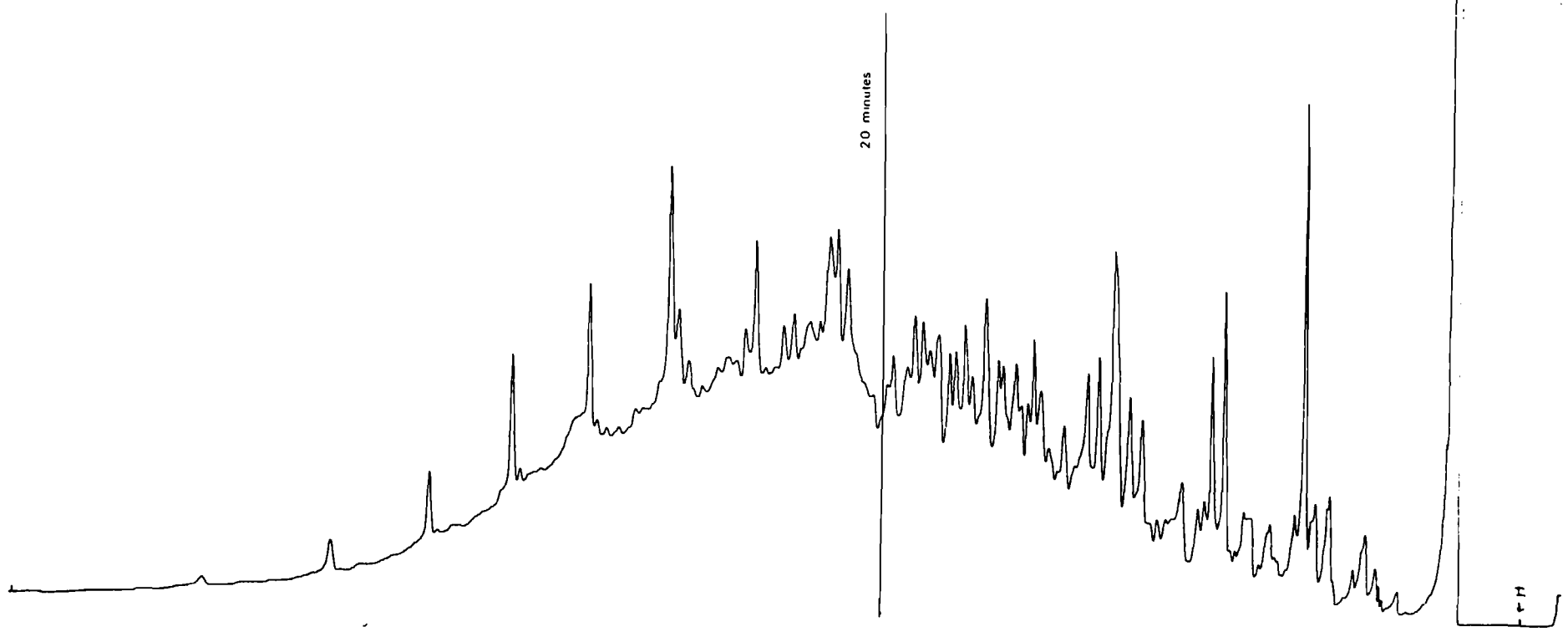


Figure 55 GAS OIL

c) Pentane extract (10%) (cleaned up with Florisil)

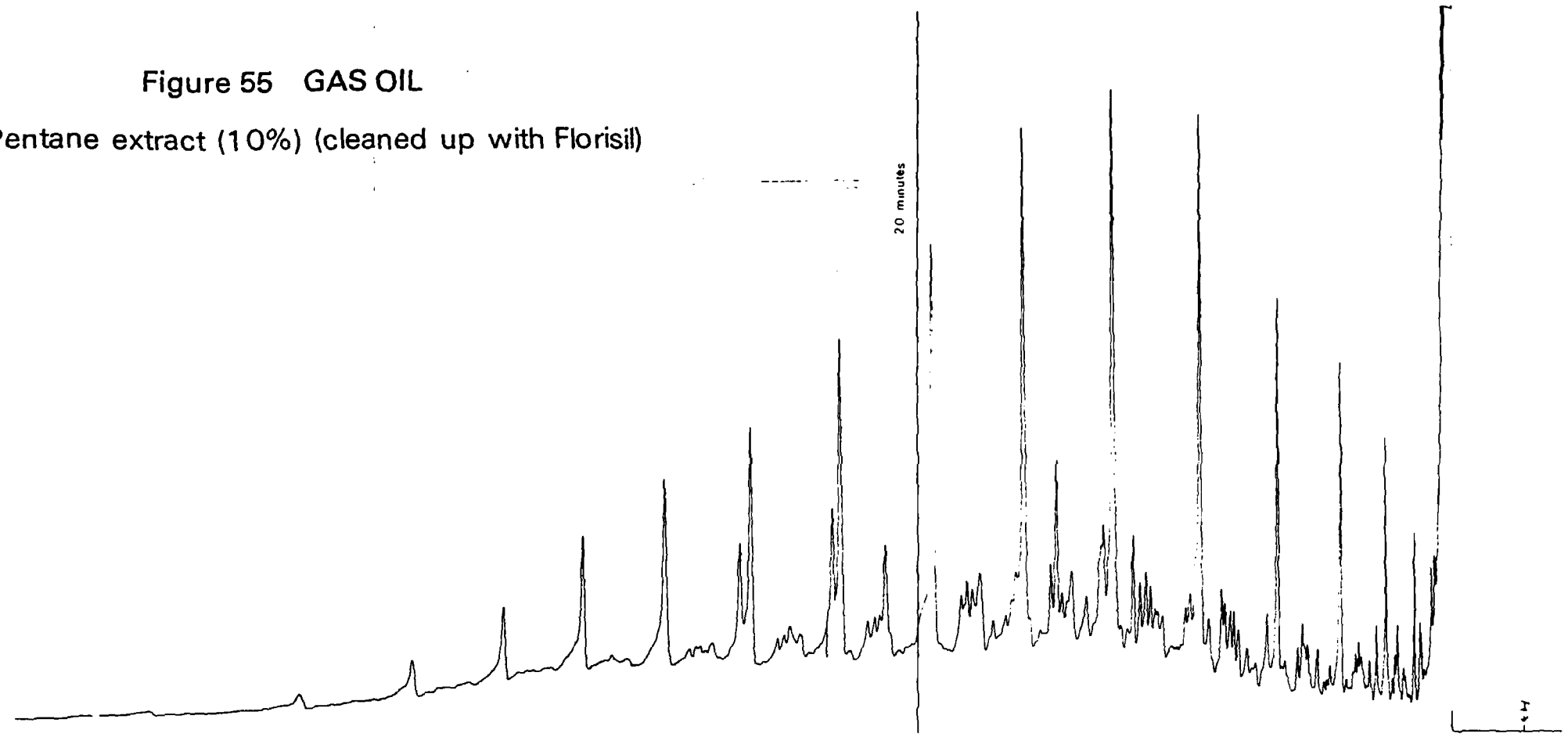


Figure 57 CREOSOTE BLENDED FROM HIGH AND LOW TEMPERATURE TARS

c) Pentane extract (10%) (cleaned up with Florisil)

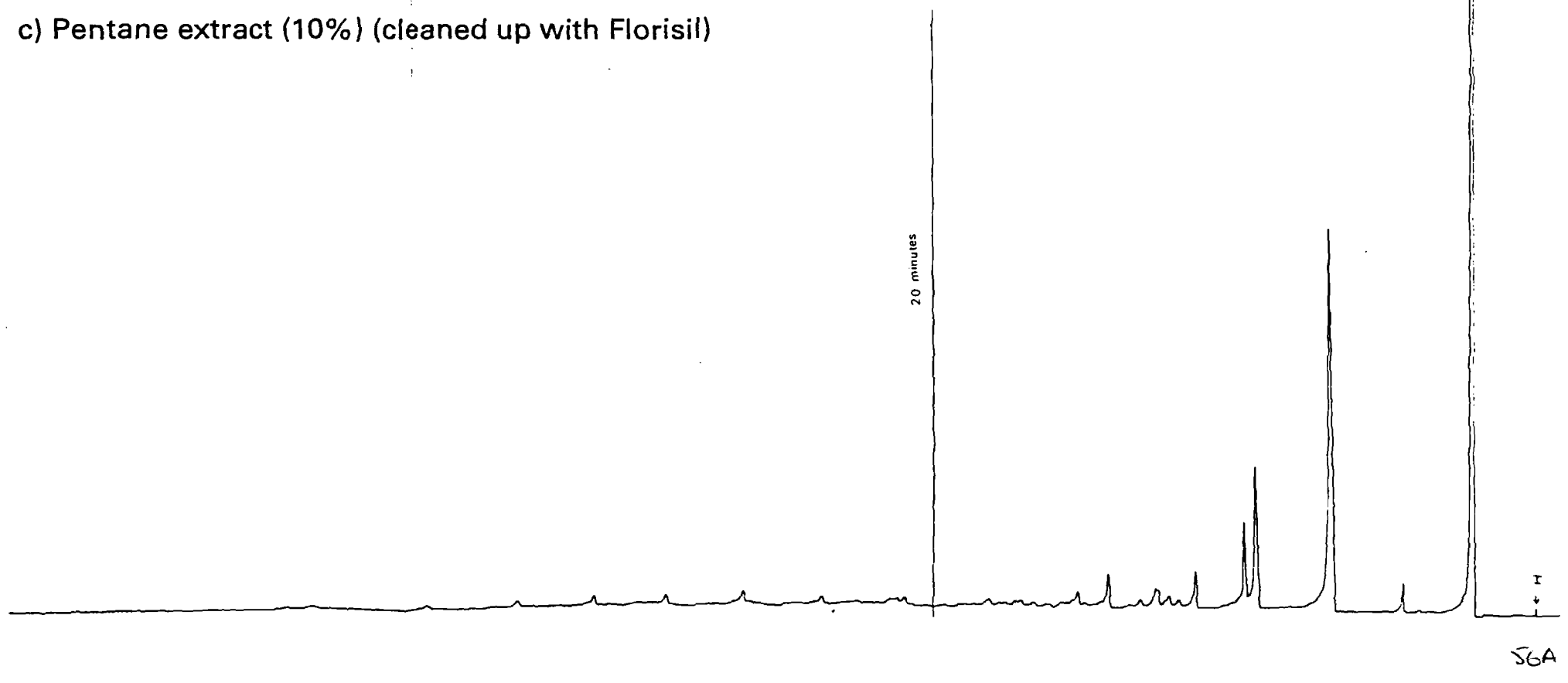


Figure 58 CREOSOTE BLENDED FROM HIGH AND LOW TEMPERATURE TARS

b) 10% Distillate in Pentane

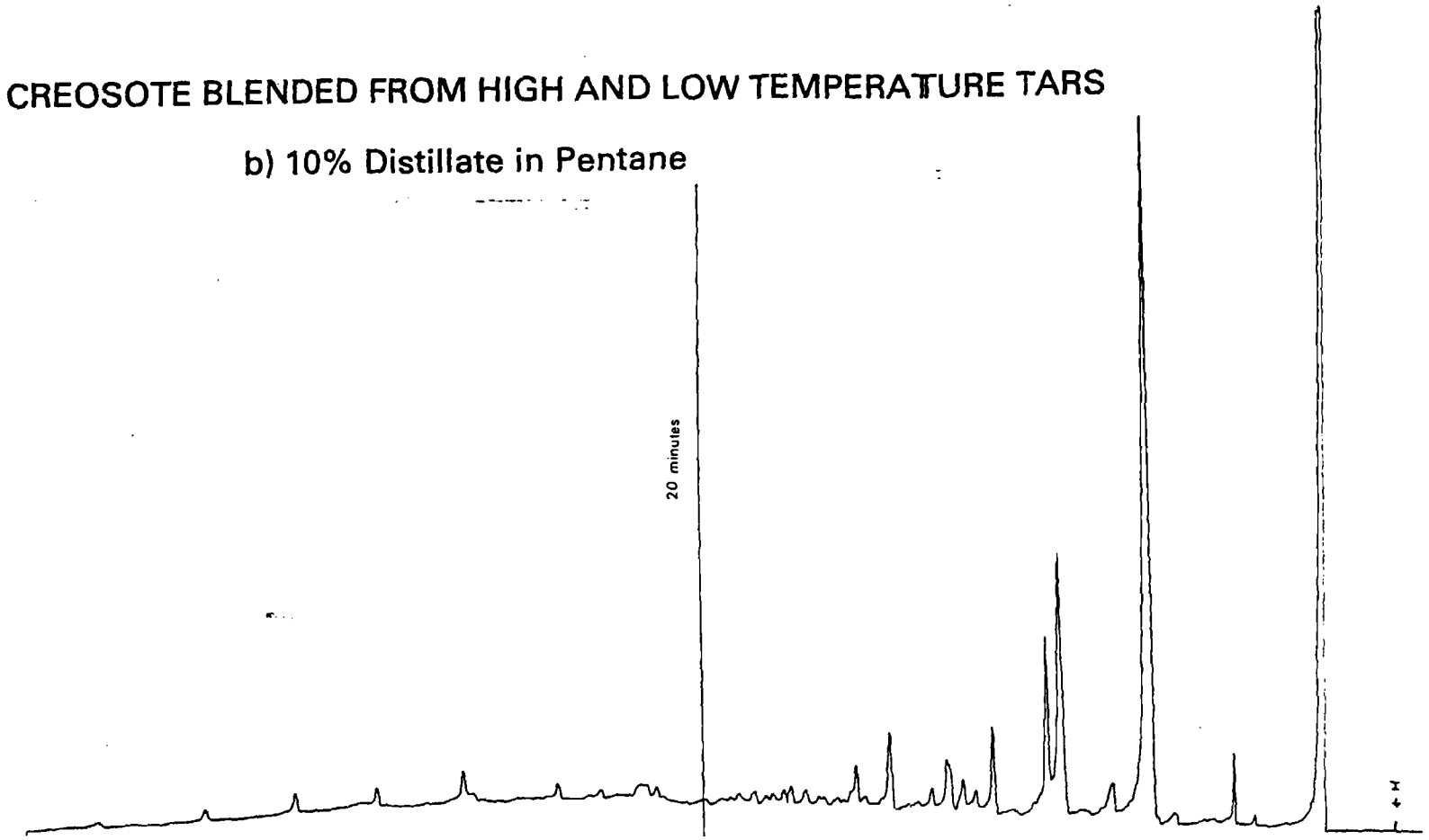


Figure 60 CREOSOTE BLENDED FROM LOW TEMPERATURE TAR

a) Distillate

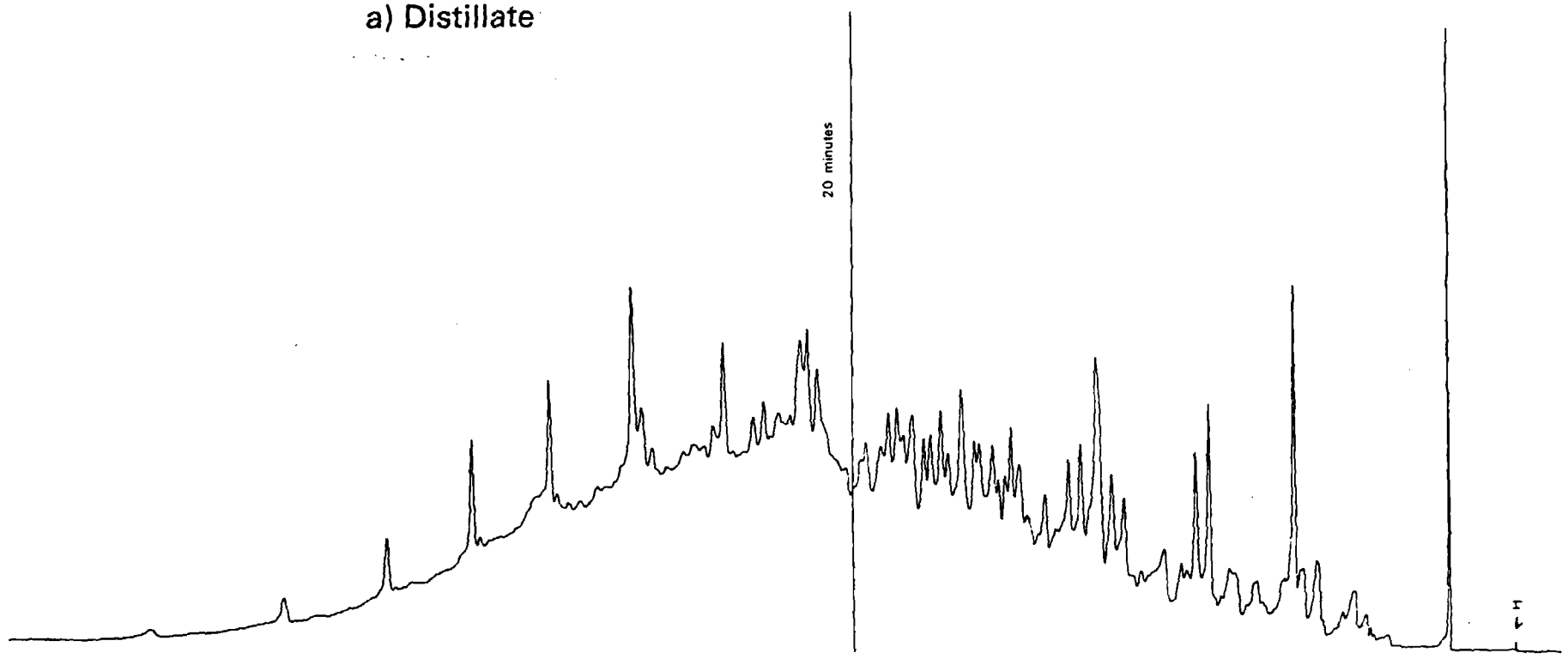


Figure 59 HEAVY FUEL OIL

b) 10% Distillate in Pentane

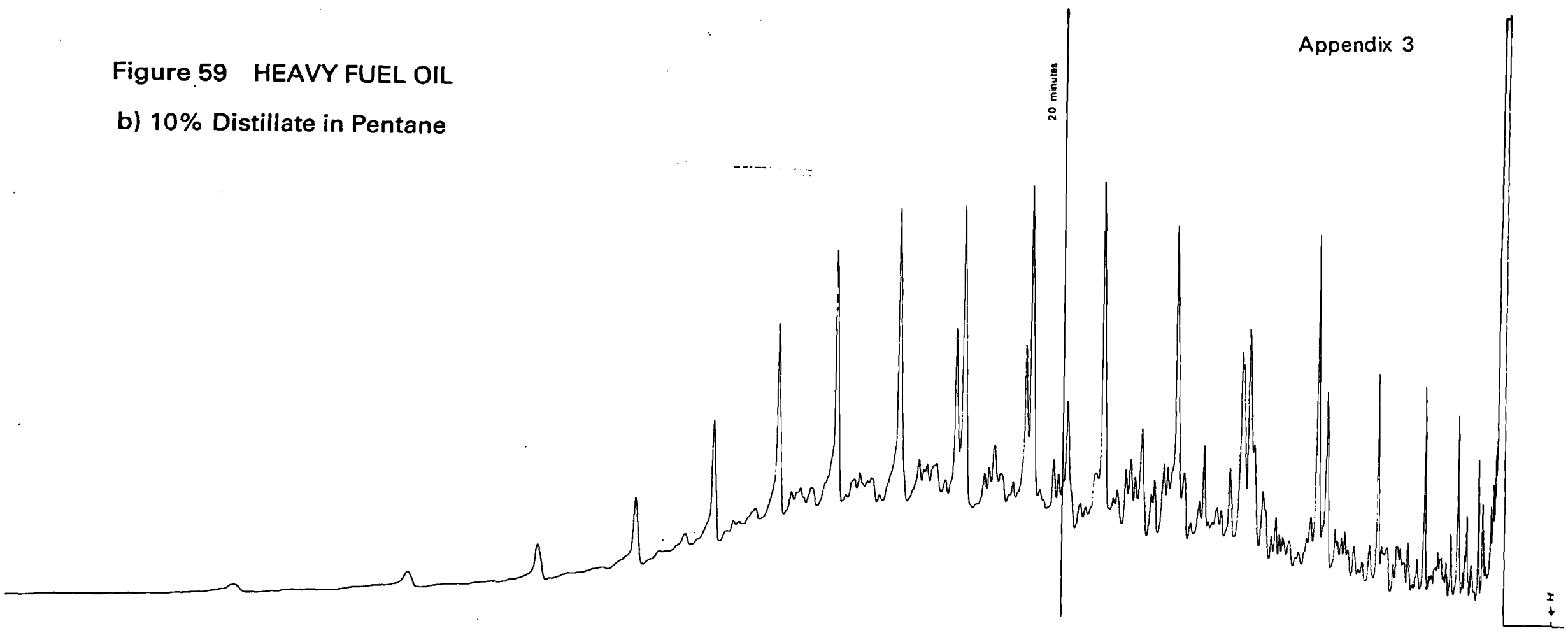
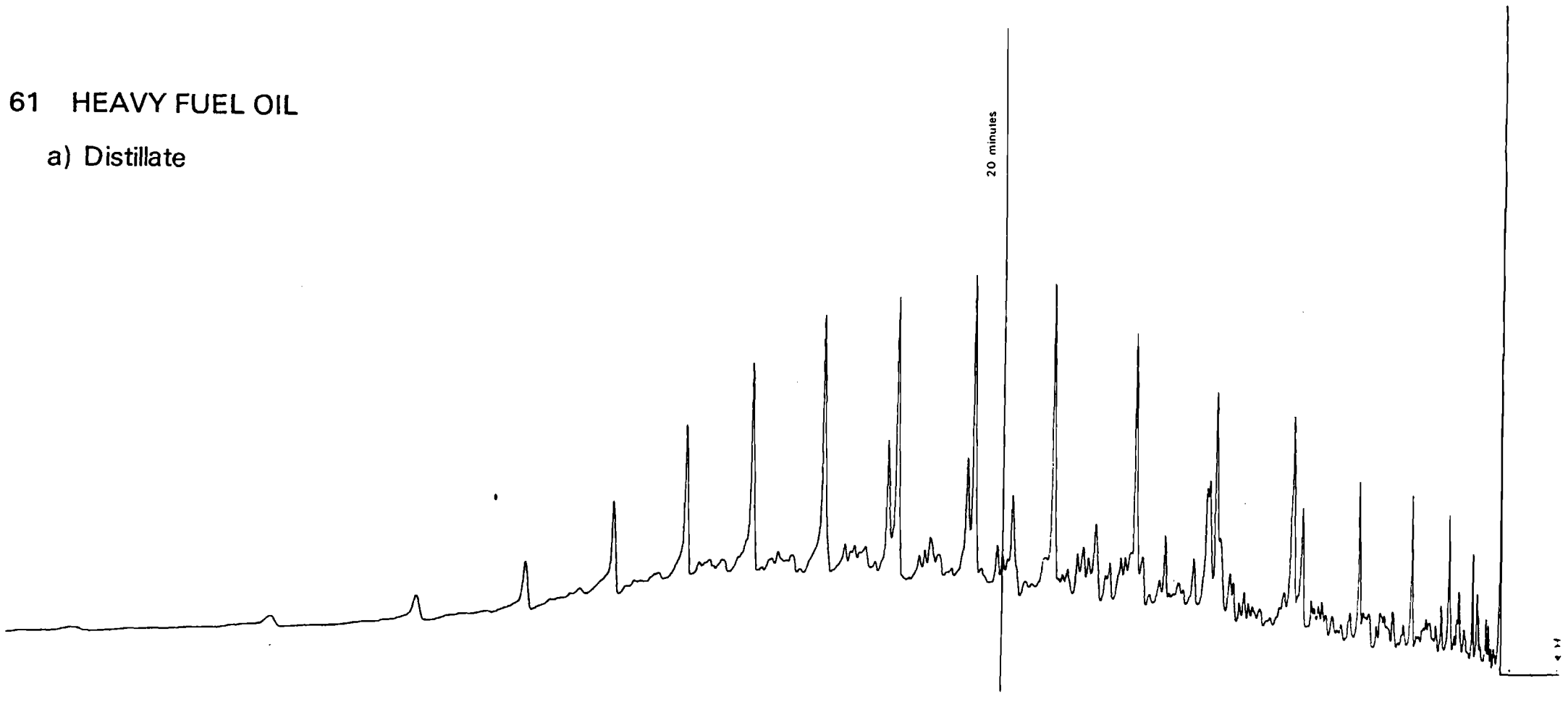


Figure 61 HEAVY FUEL OIL

a) Distillate



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(2) Macneil, D. *'Coal Carbonization Products.'* Pergamon Press, Oxford, 1966. (Re-printed by British Carbonization Research Association, the British Tar Industries Research Association may handle this publication after 1983).

(3) Royal Society of Chemistry, Analytical Division, Analytical Methods Committee. Essential Oils Sub-Committee. *Application of gas chromatography to the analysis of essential oils by temperature programmed gas liquid chromatography using a Carbowax 20M stationary phase.*

(4) International Organization for Standardization (ISO). *Animal and vegetable fats and oils – Analysis by gas liquid chromatography of methyl esters of fatty acids.* ISO – 5508 – 1978 (E).

(5) Ibid. Ref. 4 *Animal and vegetable fats and oils – preparation of methyl esters of fatty acids.* ISO – 5509 – 1978(E).

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(7) Whittle, P. J. *Analyst*, 1977, **102**, 976.

(8) *A Comprehensive Scheme for the Identification of Oils, Fats, Waxes and Tars* (to be published in this series), HMSO.

(9) *Gas Chromatography – an Essay Review 1982* (also published in this series), HMSO

(10) *Classical Methods for the Characterization of Oils, Fats and Waxes by Iodine, Hydroxyl, Saponification and Acid Values 1983* (also published in this series), HMSO.

Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this method are requested to write to:

The Secretary
The Standing Committee of Analysts
The Department of the Environment
Romney House
43 Marsham Street
London SW1P 3PY
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Standing Committee of Analysts

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