Analysis of Hydrocarbons in Waters—A Review, and An Ultra-Violet Fluorescence Spectrometric Method 1988

Methods for the Examination of Waters and Associated Materials

Her Majesty's Stationery Office

Analysis of Hydrocarbons in Waters—A Review, and an Ultra Violet Fluorescence Spectrometric Method 1988

Methods for the Examination of Waters and Associated Materials

This booklet consists of three parts

(i) The Determination of Hydrocarbons in Saline Waters by Solvent Extraction and Ultra-Violet Fluorescence Spectrometry.

(ii) A Guide to Methods Relating to the Analysis of Oils, Fats, Waxes and Tars.
(Note, one booklet also contains methods for chlorinated hydrocarbon solvents. Information on these compounds given in this booklet is also summarised).

(iii) Analysis for Hydrocarbons with over Thirty Carbon Atoms per Molecule—a Note

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Her Majesty's Stationery Office

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About This Series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, 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 These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print.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 series of booklets on single or related topics; 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 and notes 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 technical staff 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 Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has 9 Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage Works Control 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.

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 and minor additions to published booklets not warranting a new booklet 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 that booklet.

L R PITTWELL
Secretary and Chairman

11 August 1988

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 for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. 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. 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. Lone working, whether in the laboratory or field, should be discouraged.

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 check-list, 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. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. 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.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Guide to Safe Practices in 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.

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 radiochemical 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. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

The Determination of Hydrocarbons in Saline Waters by Solvent Extraction and Ultra-violet Fluorescence Spectrometry

Introduction

Mineral oil is a complex mixture containing many thousands of compounds, including both aliphatic and aromatic hydrocarbons. No single analytical method has so far been devised which can detect and quantify all of these compounds over the whole boiling range of materials encountered. In general methods are divided into those which measure a specific function of a range of compounds (such as the measurement of absorbance of energy in the infra-red region due to C-H stretching of aliphatic bonds in IR spectrophotometry) or those which allow the detection of single compounds (such as gas chromatography). There is a requirement for both types of methods as those of the latter type are usually much more time-consuming than the former, mainly due to the necessity of sample clean-up prior to analysis. The use of a rapid but less specific technique as a first or screening technique can reduce the need for such a large number of analyses to be made by the more rigorous methods by indicating which samples contain high and low concentrations of particular entities. Ultra-violet fluorescence spectrometry (UVF) is now widely used in the marine field because of its high sensitivity, ease of use, and minimal clean-up requirement. It is not specific for petroleum hydrocarbons, however, being sensitive to all aromatics, particularly those with multiple fused rings (polycyclic aromatic hydrocarbons; PAH). PAH derived from the combustion of fossil fuels and entering the oceans via atmospheric deposition will also be detected by UVF and the relative contributions of these and other sources (such as biogenic production) can only be assessed using the lengthier but more specific techniques. As there is no absolute measure of fluorescence emission it is also necessary to choose something against which to calibrate UVF measurements. In the field of oil pollution it has been usual to calibrate using a single oil, usually a whole or topped crude oil. Although batches of a single oil may vary somewhat in aromatic composition and hence fluorescence characteristics, this is usually insignificant compared to the orders of magnitude variations in concentration found in, for instance, oil spill investigations. It should also be remembered in this context that refined products, as they are usually derived from distillation cuts of crude oil, do not normally exhibit fluorescence across such a wide range. Indeed portions of the fluorescence spectrum may be entirely absent. It would not therefore be appropriate, for instance, to measure concentrations of gasoil or diesel fuel against a crude oil standard at excitation and emission wavelengths suitable for detection of the crude oil. If these limitations are borne in mind, however, UVF is an extremely useful technique, with sufficient sensitivity to be applicable for measurements of total hydrocarbon concentrations in essentially unpolluted offshore and shelf sea waters, which are generally 1 microgram per litre or less.

1. Performance Characteristics of the Method

1.1	Substance determined	Those substances extracted by pentane (or hexane) under the conditions used in the method and which fluoresce at the excitation and emission wavelengths selected.
1.2	Type of Sample	Saline waters (estuarine, coastal and shelf-sea waters).
1.3	Basis of Method	The water is extracted with pentane and the solvent extract dried and analysed by fluorescence spectroscopy.

1.4	Range of Application	Within the linear range of the spectrofluorimeter (typically 0 to 10 μg/mL in the analysed solution), though extracts may be diluted to bring them within this range. 10 μg/mL is equivalent to 18.5 μg/L in a 2.7 L sample extract reduced to 5 mL.

1.5 Standard Deviation

Ekofisk Oil Concentration μg/L [§]	Standard Deviation within-batch μg/L	Degrees of Freedom
[†] 16.7	0.73	4
THC* **μg/L** [§]	**Standard Deviation μg/L**	**Degrees of Freedom**
[‡] 2.2	0.19	8

* THC—Total Hydrocarbon Concentration (Both sets of results were obtained using pentane as extraction solvent).
[†] Extracted seawater spiked with Ekofisk crude oil.
[‡] Seawater from the NE coast of England.
[§] Concentration in the original sample.

Results obtained by: R J Law
MAFF Fisheries Laboratory
Burnham-on-Crouch
Essex CM0 8HA
who may be contacted for further information.

1.6	Limit of Detection	0.49 μg/L (with 10 degrees of freedom). (This figure obtained using a Perkin-Elmer LS-5 luminescence spectrometer, and based on replicate blank extractions).
1.7	Sensitivity	When calibrated in the range 0 to 10 μg/L of Ekofisk crude oil, a concentration of 0.01 μg/mL may be determined. This is equivalent to 0.02 μg/L of oil in a 2.7 L sample extract reduced to 5 mL, but in practice results are quoted to only 1 decimal place. (These figures may be instrument dependent and are for a Perkin-Elmer LS-5 model).
1.8	Bias	Recoveries of Ekofisk crude oil from water were 96 ± 4% at 16.7 μg/L.
1.9	Interference	Any material extracted by the solvent and which fluoresces at the excitation and emission wavelengths selected.
1.10	Time Required for Analysis	1 hour to obtain a result from collection or receipt of a sample assuming that instrument calibration has already been carried out. 12 man-hours has proved sufficient time for the collection and analysis of 40 samples at sea.

2 Principle

The hydrocarbons are extracted by liquid-liquid extraction into pentane (or hexane). The extract is dried over anhydrous sodium sulphate.

The hydrocarbon concentration is determined by measurement of the flourescence emitted at 360 nm whilst the sample is excited at 310 nm, by comparison with the fluorescence of a standard solution of Ekofisk crude oil under the same conditions. The range of aromatic hydrocarbons present in the sample is established by synchronous excitation/emission scanning and compared with that of the oil used for calibration to confirm that it is appropriate. A simple filter fluorimeter may be used to obtain a quantitative measurement, but at the expense of such confirmation.

Other excitation/emission wavelength combinations may be used if particular oils are to be determined; 270/330 nm for instance being used for diesel oil (gasoil) determinations. If the oil to be determined is known and available, it may be used to prepare standards.

3 Interferences

In practice, interferences have proved to be few; although if the intention is to determine the extent of hydrocarbon oil pollution, then the presence of combustion derived or naturally produced polycyclic aromatic hydrocarbons would represent an interference.

The use of synchronous excitation—emission spectroscopy can sometimes highlight such interferences, but more detailed investigation may be necessary using techniques such as gas chromatography or coupled as chromatography/mass spectrometry.

4 Hazards

Pentane and hexane are both volatile and highly flammable, and both act as narcotics. Threshold limit values (TLV's) are 500 ppm (1500 and 1800 mg/m^2 respectively). It may be prudent to limit exposure to both solvents by working in a well-ventilated room or under an efficient fumehood.

5 Reagents

5.1 Pentane (or hexane) Distilled-in-glass grade:— fluorescence or other grades may be adequate.

5.2 Anhydrous Sodium Sulphate:— Analytical reagent grade.

5.3 Ekofisk crude oil (other oils may be used for standardization if required; single compounds such as chrysene or pyrene are also sometimes used).

5.4 Standard solutions of Ekofisk crude oil. A convenient stock standard of 2000 μg/mL may be prepared by weighing 200 ± 5 mg of Ekofisk crude oil into a 100 mL volumetric flask and diluting to volume with pentane. If weighed after preparation and after use, stored in a spark-proofed refrigerator at 4°C and made up to weight with pentane before subsequent use, this stock solution can be kept for up to 2 months. Working standards within the range 0 to 10 μg/mL can be prepared using a capillary micropipette and various sizes of volumetric flasks, and should be freshly made each day. In order to prevent contamination of the standards, the micropipette should be of the type in which only glass and PTFE contact the material being pipetted, and it should be solvent cleaned before use as should all glassware.

6 Apparatus

6.1 A glass separating funnel of 3 litre capacity, with PTFE stopcock and glass stopper. A cylindrical funnel of this size is easiest to handle, particularly on board a ship.

6.2 A spectrofluorimeter capable of synchronously scanning both excitation and emission monochromators whilst maintaining a fixed offset between them.

6.3 A rotary film evaporator with water bath, which can be thermostatically controlled in the range 25 to 30°C. A Kuderna-Danish evaporator should also be suitable.

6.4 Standard laboratory glassware.

7 Sample Collection and Preservation

The collection of representative and uncontaminated samples of water for hydrocarbon analysis at trace levels is not straightforward, and reference should be made to a general text on sampling (1). (A sampler for use in marine and estuarine situations is shown in Figure 5 therein). A modified version of this sampler has also proved suitable for collection of samples down to depths of 50 m when deployed from a hydrowire. (2).

Extractions should if possible be carried out immediately, but if this is not possible then the sample should be stored in a refrigerator at 4°C. Even at this temperature some alteration is inevitable and extractions should be carried out as soon as possible after sample collection. Sample extracts may be stored in glass containers with PTFE cap liners at −20°C for many months.

8 Analytical Procedure

Step	Procedure	Notes
8.1	Extraction	
	Pour the sample liquid from the sample bottle into a 3 L separating funnel, previously cleaned with pentane. (See note (a)).	(a) For marine and estuarine work a 2.7 L sample is usual, taken in a glass Winchester bottle. (See (2)). Larger or smaller volumes (1 to 10 L), may be collected where particularly high or low concentrations are expected. Samples should not be divided for analysis so as to avoid errors introduced where hydrocarbons adhere to the interior walls of the sampling bottle.
8.1.2	To the sample bottle add 50 ± 1 mL of pentane. (note (b)).	(b) Hexane may be used as an extractant.
8.1.3	Swirl the sample bottle so as to wash pentane over all the inside surfaces. Then pour the pentane into the separating funnel.	
8.1.4	Replace the glass stopper and shake the separating funnel vigorously for five minutes. Allow the layers to separate.	
8.1.5	Run off the lower aqueous layer into the sample bottle.	
8.1.6	To a 100 mL conical flask previously cleaned with pentane add 6 ± 1 g anhydrous sodium sulphate. (note (c)).	(c) Coastal and estuarine samples which form emulsions may require the addition of more sodium sulphate to remove all the water.
8.1.7	Run off the pentane extract into the conical flask.	
8.1.8	Repeat steps 8.1.1 to 8.1.4 with a new aliquot of pentane.	
8.1.9	Run off the aqueous layer into a measuring cylinder and note the volume (V_1 mL).	
8.1.10	Run off the second pentane extract into the conical flask and seal with a glass stopper. Swirl the conical flask to thoroughly mix the contents and leave to stand for at least 10 minutes.	
8.1.11	Decant the extract into a pentane-cleaned 250 mL round-bottomed flask suitable for attachment to the rotary evaporator.	

Step	Procedure	Notes
8.1.12	Add 10 ± mL of pentane to the conical flask, swirl, and decant into the round bottomed flask.	
8.1.13	Concentrate the extract to a final volume of 1 to 2 mL by means of the rotary evaporator. The water bath should be set to maintain a temperature of 28 ± 1 °C. (note (d)).	(d) This is to minimize losses of low-boiling hydrocarbons.
8.1.14	Transfer the concentrated extract quantitatively, by means of a Pasteur pipette, to a volumetric flask (V_1 mL) and make up to volume. (note (e)).	(e) For marine samples 5 or 10 mL would be a suitable volume for an extract of 2.7 L of water.
8.2	Fluorescence Measurement	
8.2.1	On the fluorescence spectrometer set the excitation wavelength to 310 nm and the emission wavelength to 360 nm. (note (f)). Set both excitation and emission slits to 5 nm. (note (g)).	(f) See section 2. (g) This may be instrument dependent to some extent. These slits are adequate for a Perkin-Elmer LS-5 spectrometer.
8.2.2	Using clean pentane and the standard solutions prepared as in section 5.4 construct a calibration curve in the range 0 to 10 μg/mL of oil. (see Figure 1). (note (h)).	(h) For all spectrofluorimeters investigated so far 10 μg/mL of Ekofisk crude oil has been within the linear range of the instruments.
8.2.3	Clean all cells used for calibration and refill with clean pentane. Replace in spectrofluorimeter and check that their fluorescence emission is zero. (note (i)).	(i) This technique is very sensitive and it is easy to contaminate glassware. Always check cleanliness of cells before filling with a fresh solution for measurement.
8.2.4	Measure the fluorescence emission of the sample extract (as μg/mL oil equivalents) and note the result. If the result is >10 μg/mL dilute the extract quantitatively by a suitable factor and remeasure, noting the dilution factor. Repeat if necessary until the result falls within the linear range. See Section 10. (note (j)).	(j) Other oils may be used for calibration purposes if required. A number of different crude oils have been investigated and details of their response relative to Ekofisk crude oil are given in Table 1.
8.2.5	Calculation The concentration of hydrocarbons in the original aqueous sample may be calculated from the equation: $C = \frac{V_2 F D}{V_1} - C_B$ where C = total hydrocarbon concentration (THC) in the original sample expressed as μg/l Ekofisk crude oil equivalents) V_1 = volume of original sample (litres) V_2 = volume of extract (before dilution) (mL) F = fluorescence of extract (μg/mL oil equivalents) D = dilution factor (if applicable) C_B = THC calculated for the appropriate procedural blank (See Section 9)	
8.2.6	Dilute the extract twofold and remeasure the fluorescence emission. Repeat step 8.2.5 and compare the two values for the THC. If the second value is significantly higher than the first, repeat until two consecutive results agree. (note (k)).	(k) Quenching of fluorescence emission can occur in concentrated solutions due to re-absorption of emitted light. This results in lower apparent THC values in highly concentrated solutions. The effect is eliminated by dilution.

Step	Procedure	Notes
8.3	Fluorescence Spectra	
8.3.1	Obtain the synchronous excitation-emission spectrum of the sample by scanning excitation between 230 and 500 nm and emission between 255 and 525 nm. The 25 nm offset being maintained at all points of the scan. (note (a)).	(a) Offsets within the range 8 to 30 nm are sometimes used, but 25 nm is recommended. (see Figure 2 for the effect of varying the offset).
8.3.2	Compare the synchronous spectra of sample extract and standard to check that the oil standard used gives a similar spectrum, ie, is appropriate for the samples analysed. (note (b)).	(b) See Figure 3 for examples of synchronous spectra.

9 Blanks

Complete procedural blanks should be included in each batch of analyses, and replicated if determinations are being made at concentrations <20 μg/L. Below 2 μg/L the blank value will be significant with respect to the measured concentration and the repeatability of the blank will need to be assessed for blank correction and determination of a limit of detection.

10 Change of Concentration Range of the Method.

The procedure given can be used to determine hydrocarbon concentrations in the range 0 to 18.5 μg/L without modification, for a sample volume of 2.7 L and a final extract volume of 5 mL. When higher concentrations are encountered it is recommended that the extracts are diluted with pentane and the appropriate factor used in the calculation of the result. Smaller samples may also be collected initially by the use of smaller sample bottles; subdivision and subsampling from a large sample are not recommended because of errors caused by adsorption of hydrocarbons to the inner surfaces of the sample bottles.

11 Checking the Validity of Analytical Data

Once the method has been put into routine operation many factors may subsequently adversely affect the accuracy of the analytical result. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. No suitable standard reference materials are available for use with this method, and whilst spike and recovery techniques may be usefully applied, the added oil is unlikely to be accommodated in the spiked sample as it would be naturally. For this reason it is also recommended that analysts take the opportunity to intercalibrate their analyses with those of other workers whenever possible. Examples of such exercises using similar methods are in the literature (3,4,5). The recovery of a pentane spike of Ekofisk crude oil is a useful check on the efficiency of recovery. If quantitative recovery cannot be demonstrated the calibration procedure outlined in this method is invalid, and calibration should be carried out by spiking and extraction of extracted seawater samples.

Before firmly recommending this method for general use it is desirable to know the accuracy achievable in other laboratories. It would, therefore, be of great value if any laboratory using or considering the use of this method could estimate the accuracy of its own analytical results and report the findings to the Secretary of the Department of the Environment's Standing Committee of Analysts (See Section 12).

12 Address for Correspondence

However thoroughly a method may be tested there is always the possibility of a user encountering a hitherto unreported problem.

Correspondence about these methods should be addressed to:—

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

13 References

(1) Sampling of Oils, Fats, Waxes and Tars in Aqueous and Solid Systems 1983. HMSO, London.

(2) Law R J, Fileman T W and Portmann J E (1988). Methods of analysis for hydrocarbons in marine and other samples. Aquat. Env. Prot.: Analyt. Meth., MAFF Direct, Fish, Res., Lowestoft. No 2.

(3) Anonymous (1982). Proceedings of a Workshop on the Analysis of hydrocarbons in seawater, March 23–April 3, 1981. Baltic Sea Environment Proceedings No 6. Helsinki Commission, 52 pp.

(4) Knap A H, Burns K A, Dawson R, Ehrhardt M and Palmork K (1986). Dissolved /dispersed hydrocarbons, tarballs and the surface microlayer: Experiences from an IOC/UNEP workshop in Bermuda, December 1984. Mar. Pollut. Bull., *17*, 313–319.

(5) Law R J, Marchand M, Dahlmann G and Fileman T W (1987). Results of two bilateral comparisons of the determination of hydrocarbon concentrations in coastal seawater by fluorescence spectroscopy. Mar. Pollut. Bull., *18*, 486–489.

Table 1 Variations in the fluorescence response of different crude oils at 310/360 nm.

Crude Oil	Fluorescence Intensity
Ekofisk	1.00
Auk	0.65
Beryl	1.11
Montrose	0.80
Dunlin	1.05
Forties	0.85
Argyll	0.61
Thistle	0.86
Piper	0.91
Claymore	0.98
Murchison	0.79
Ninian	0.85
Brent	0.74
Beatice	0.77
Kuwait	0.80
Light Arabian	0.78
Light Iranian	0.99
Light Saudi Arabian	0.82
Nigerian	1.10
Murban (Abu Dhabi)	0.63
Brega (Libya)	0.86
ARAMCO Arabian Light	0.82
Romashkino	1.10*
Russian crude oil	0.83† (exact identity unknown)

Oil samples supplied by the Warren Spring Laboratory, except:—
* supplied by Eeva-Liisa Poutanen, Institute of Marine Research, Helsinki, Finland.
† supplied by Jarle Klungsøyr, Institute of Marine Research, Bergen, Norway.

All analyses conducted at the MAFF Fisheries Laboratory Burnham-on-Crouch, Essex.

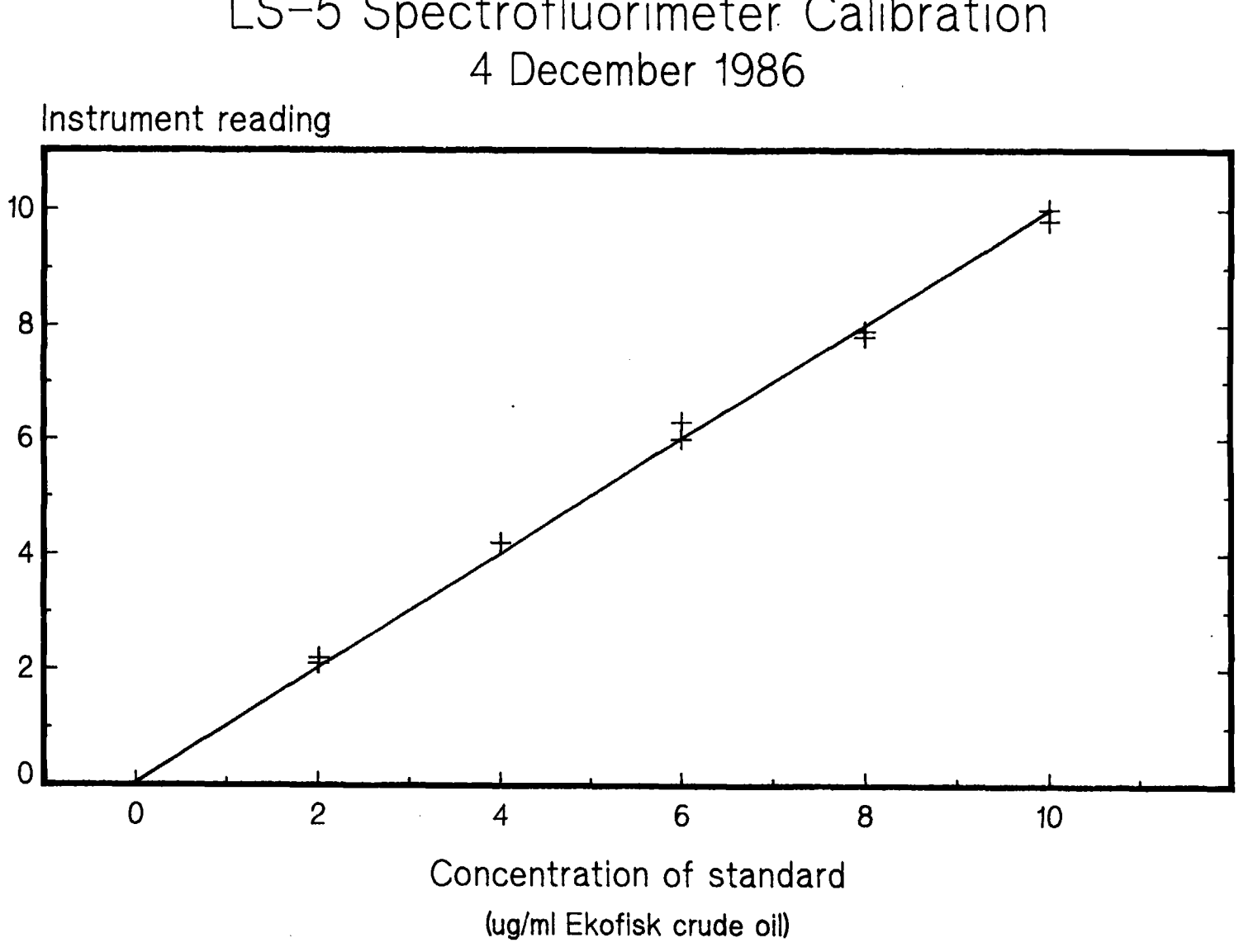


Figure 1. Example of calibration of a Perkin-Elmer LS-5 luminescence spectrometer in the linear range (0 to 10 ug/mL Ekofisk crude oil in pentane). Solutions were prepared in duplicate.

Fig 2a

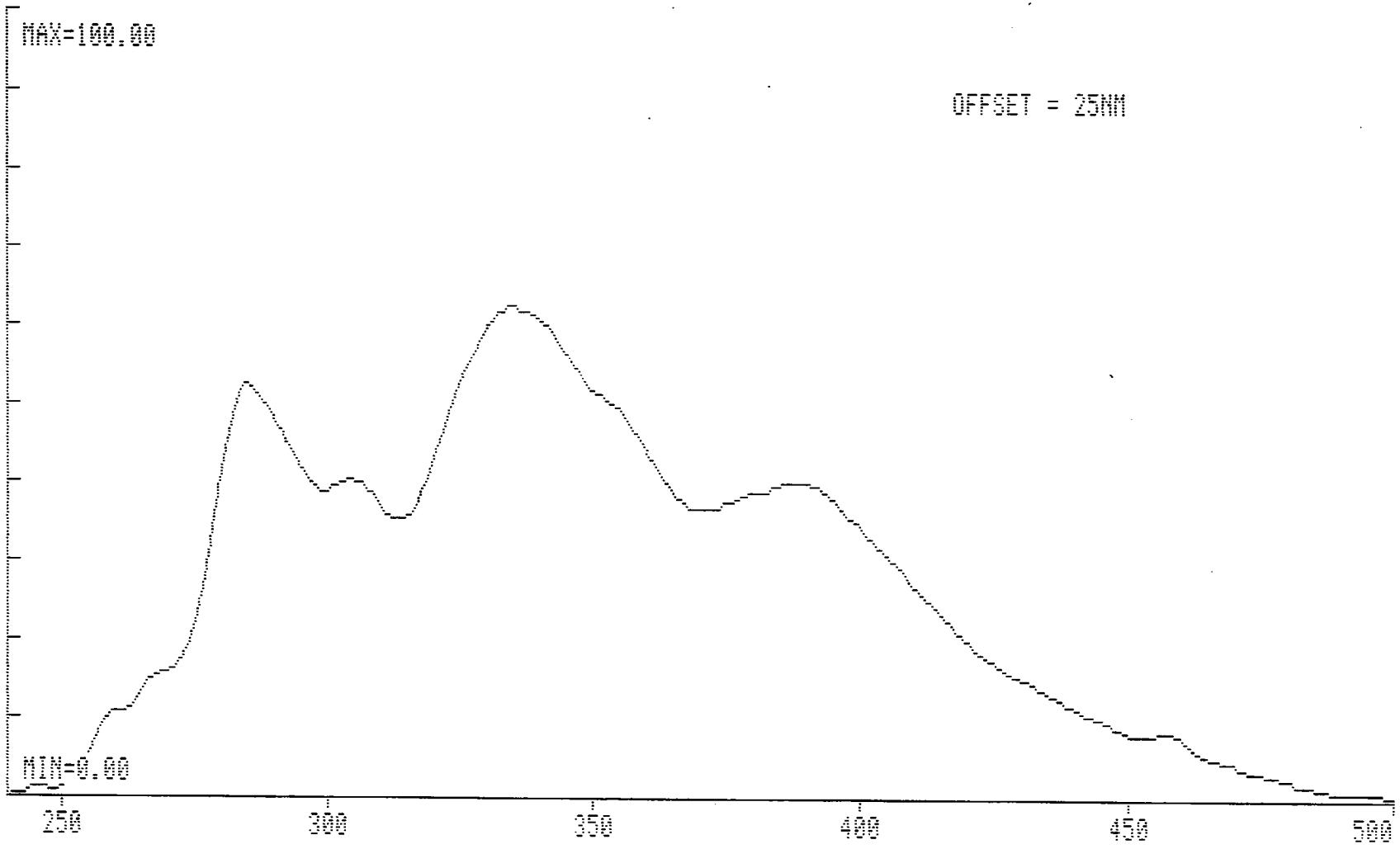


Figure 2. Variations in the synchronous spectrum of ARAMCO Arabian light crude oil with varying offset:
(a) 25 nm
(b) 20 nm
(c) 15 nm
(d) 10 nm
The concentration in each case was 10 ug/mL.

Fig 2b

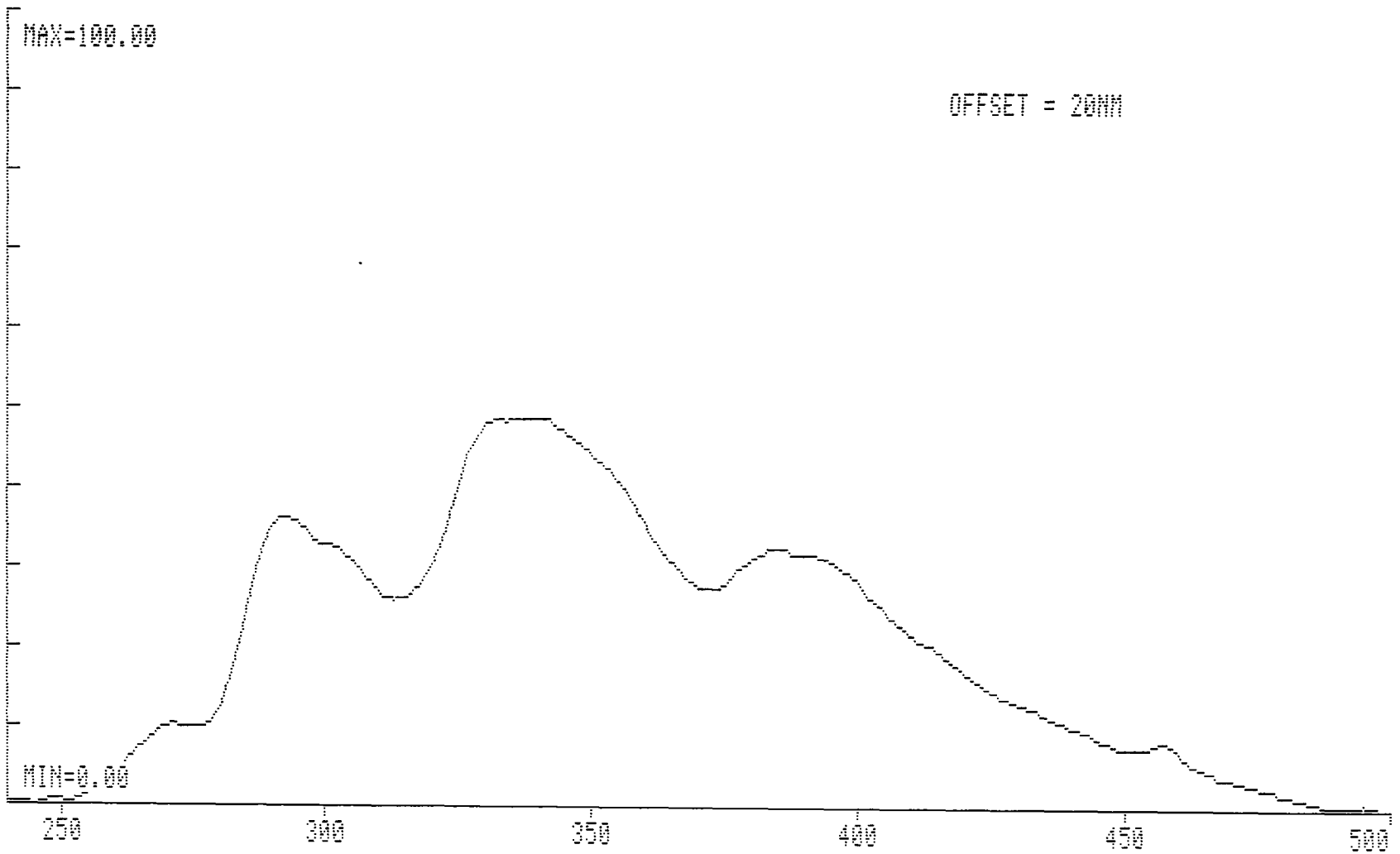


Fig 2c

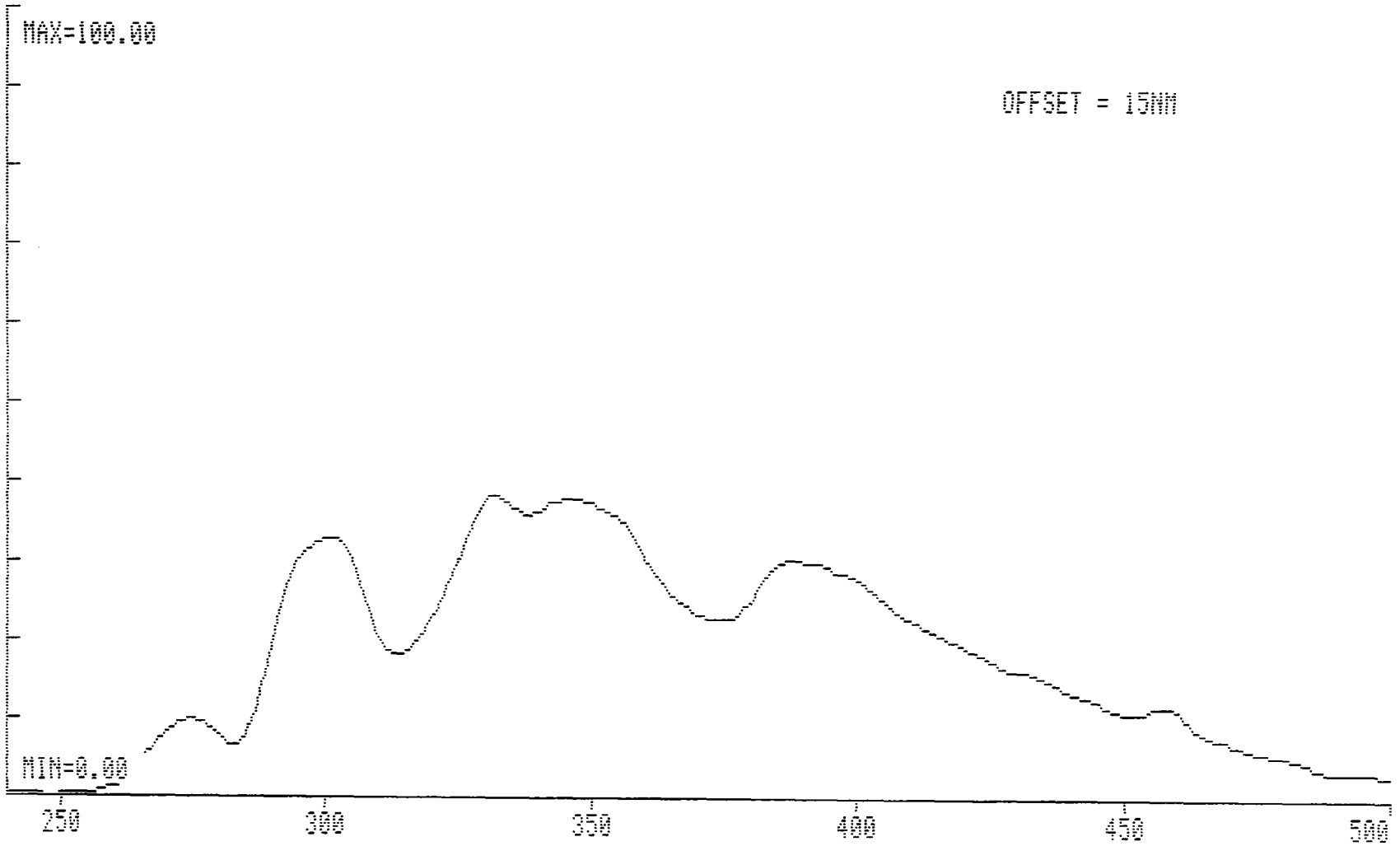


Fig 2d

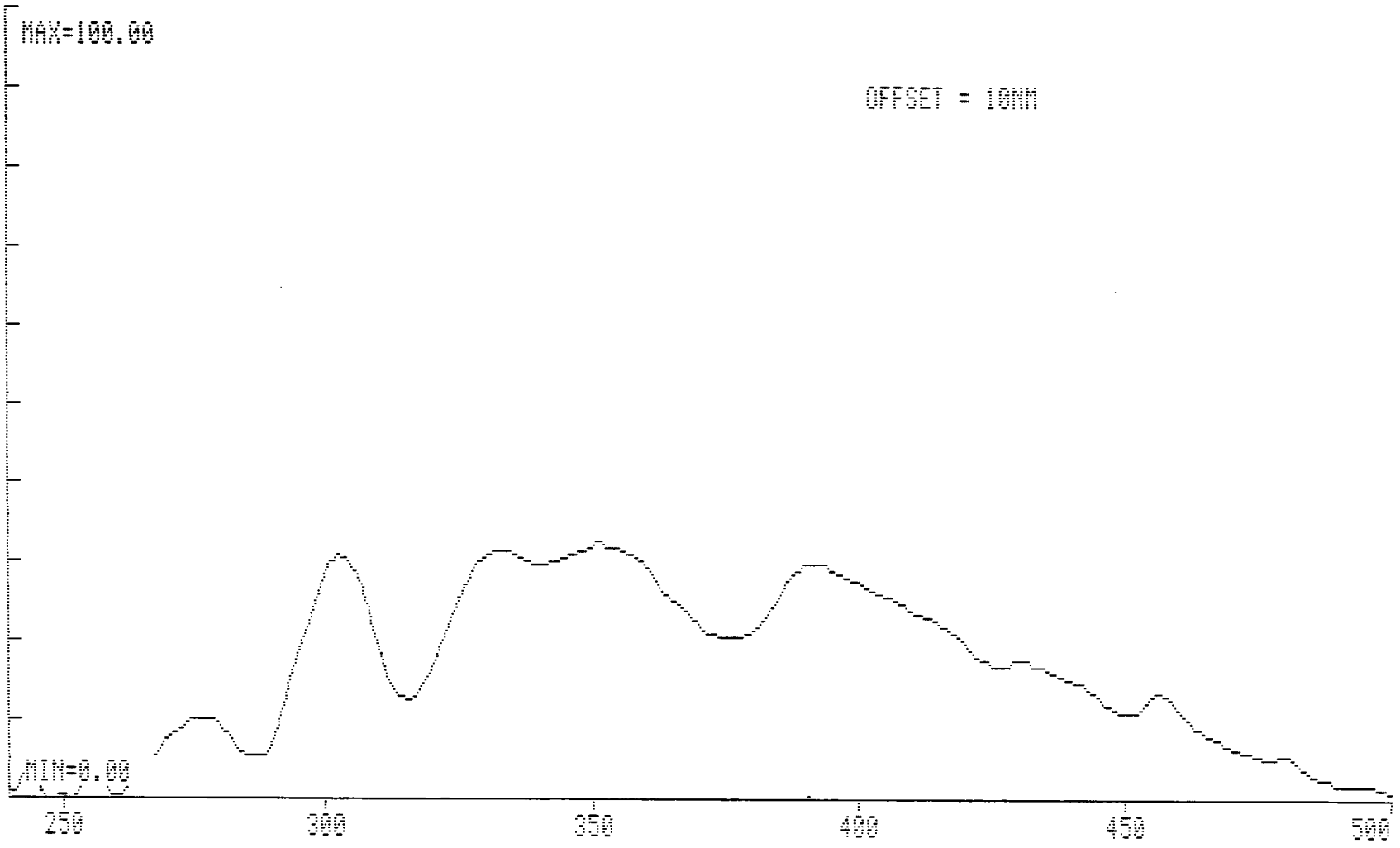


Fig 3a

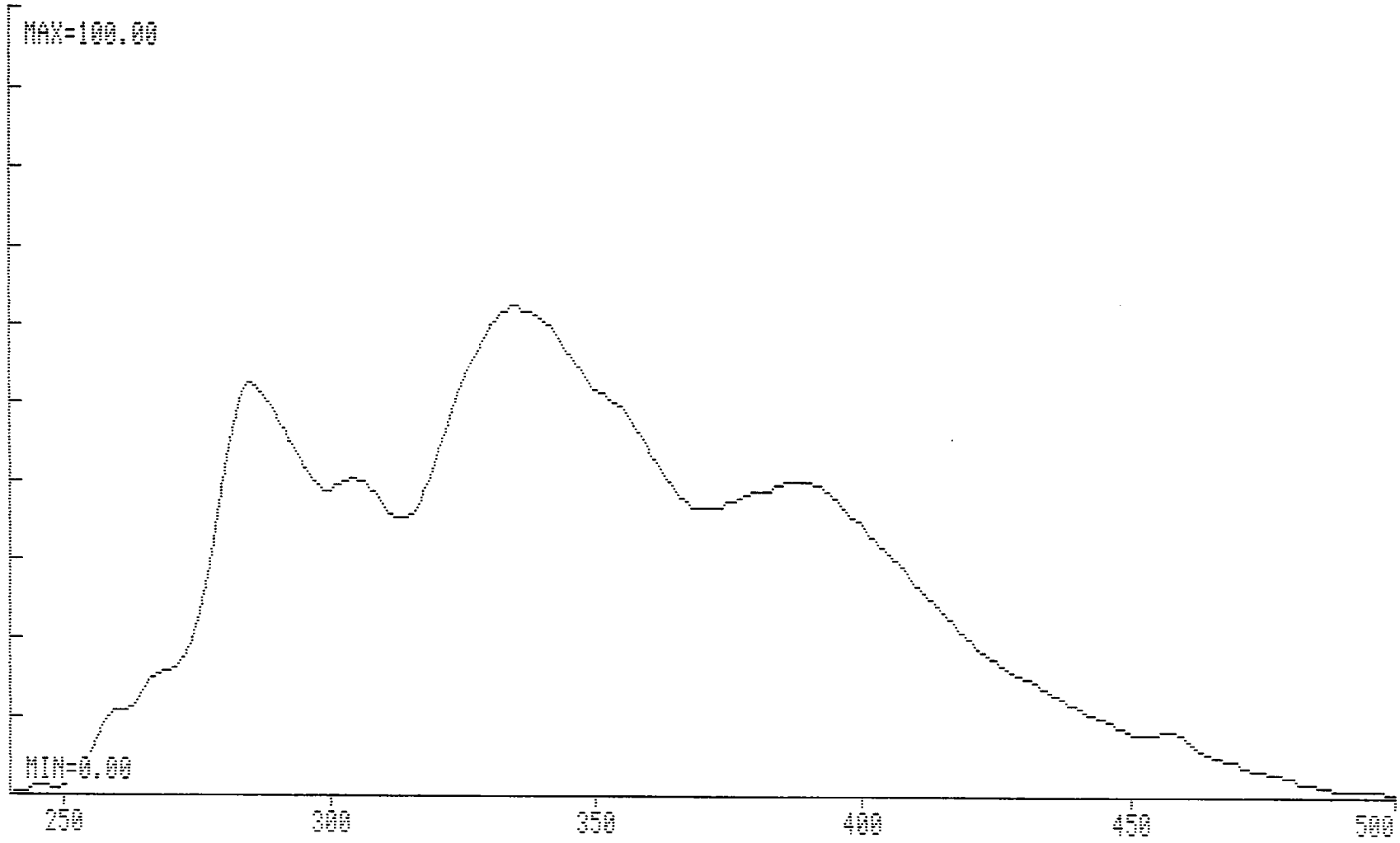


Figure 3. Synchronous spectra obtained for different oils under the standard conditions with an offset of 25 nm:

(a) ARAMCO Arabian light crude oil
(b) Ekofisk crude oil
(c) diesel oil (gasoil)

The concentration in each case was 10 ug/mL.

Fig 3b

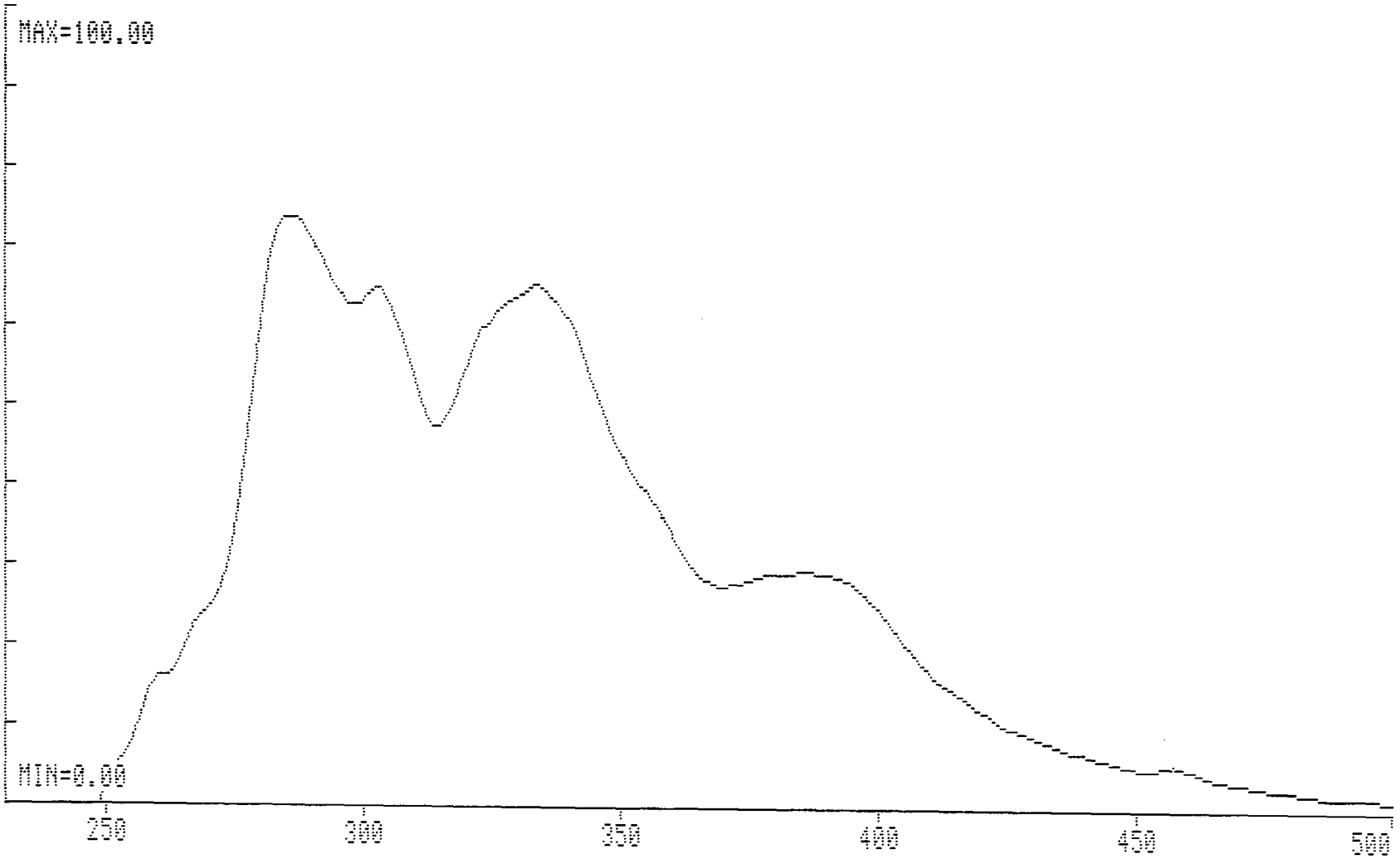
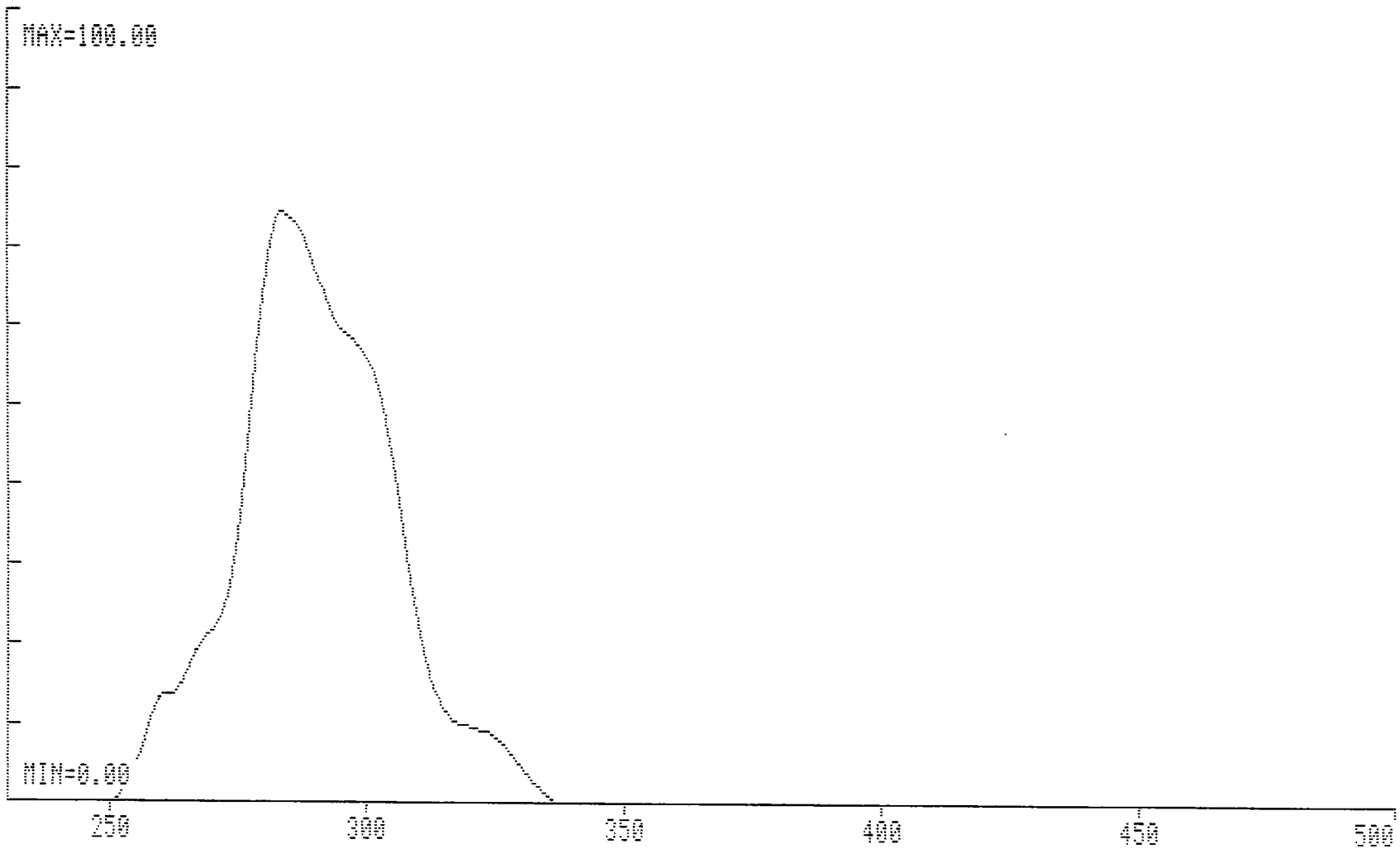


Fig 3c



A Guide to Methods relating to the analysis of Oils, Fats, Waxes and Tars

List of Methods Published in this series

Number in Table below	ISBN	Title
1	011 751436 5	The determination of material extractable by carbon tetrachloride and of certain hydrocarbon oil and grease components in sewage sludge, 1978.
2	011 751677 5	Gas chromatographic and associated methods for the characterization of oils, fats, waxes and tars, 1982.
Comprising		
2a		Low resolution gas chromatography—general method.
2b		Low resolution gas chromatography of methyl esters of natural oils and fats.
2c		The recovery of oil from heavily polluted water samples and the preparation of distillate and residue fractions of the oil.
2d		High resolution gas chromatography.
2e		Identification of gas oil by the isolation of chemical markers.
3	011 751729 1	Classical methods for the characterization of oils, fats and waxes by saponification, hydroxyl, iodine and acid values, 1983.
Comprising		
3a		Determination of the saponification value.
3b		Determination of the hydroxyl and acetyl values.
3c		Determination of the iodine value.
3d		Determination of the acid value.
4	011 751791 7	Thin lyer chromatographic characterisation of oils, fats, waxes and tars, 1983.
5	011 751956 1	The sampling of oils, fats, waxes and tars in aqueous and solid systems, 1983.
6	011 751728 3	The determination of hydrocarbon oils in waters by solvent extraction, infrared absorption and gravimetry, 1983.

Number in Table below	ISBN	Title
7	011 752076 4	Determination of oils and fats in waste water by filtration, solvent extraction and gravimetry, 1987.
8	011 751942 1	Material extractable by light petroleum from sewage sludge. (Tentative method) 1985.
9	011 752004 7	Determination of very low concentrations of hydrocarbons and halogenated hydrocarbons in water 1984–5.
10	In this booklet	Determination of hydrocarbons in saline waters by ultra-violet fluorescence spectrometry.
11	011 752128 0	Determination of methane and other hydrocarbon gases in water, 1988.
12	011 752032 2	The determination of 6 specific polynuclear aromatic hydrocarbons in waters (with notes on the determination of other PAH) 1985.

For additional information on other methods see pages 32–36 in this booklet.

Determinands and Use by Method

Method number	Determinand	Type of sample
1a	Those substances which are extracted from sewage sludge by carbon tetrachloride and remain after evaporation of the solvent at 105°C.	Sewage sludge
1b	Those substances in the carbon tetrachloride extract which remain in the extract after passage through silica gel and Florisil columns ie aliphatic, alicyclic and some mono-aromatic hydrocarbons.	Sewage sludge
2a	Oil of petroleum origin; other natural oils and tars may be broadly determined	liquid, semi-liquid, solid or concentrated extract
2b	Natural oils and fats	Oil or fat or extracted material from which solvent has been removed
2c	Separation of water, extraneous matter, oil and distillate and residue fractions of oil sample	grossly polluted water samples
2d	Petroleum oils, coal tar and related neutral fractions, low boiling fraction (from 2c above) of oil residues	liquid or solvent solutions of petroleum oils, coal tar and neutral fractions
2e	Chemical markers in duty-free gas oils (CI Solvent Red 24 and quinizarin)	Diesel oil from pollution samples
3a	Saponification value denotes the number of mg potassium hydroxide which is required to saponify 1g of fat or oil ie to neutralize the free fatty acids and the fatty acids combined as glycerides.	Animal and vegetable oils and fats. Modifications to procedures are given for application of the method to wool grease and its derivatives, waxes, oxidized and polymerized oils.

Basis of method	Range of application	Limit of detection	
The sludge is extracted with carbon tetrachloride. The solvent is evaporated and the residue dried at 105°C. The material extracted is weighed.	Up to 1 g in the sample	Not determined	1a
A solution of the extract is passed columns of Florisil which removes polar materials, and through silica gel which removes most aromatic compounds. The solvent is evaporated and the residue dried at 105°C. The residue is then weighed.	Crude sewage sludge—up to 400 mg in the sample. Digested sludge—up to 1 g in the sample	Not determined	1b
temperature programmed low resolution g.c. using f.i.d. direct injection or injection of concentrated solution	1 μL of concentrated solution or 3 mg of material	qualitative method	2a
transesterification followed by temperature programmed low resolution g.c. using f.i.d.	150 mg oil or fat in 5 ml heptane	not applicable method quantifies individual components of pure oil or fat	2b
water is removed by extractive distillation with toluene and extracted oil is fractionally distilled at atmospheric and then reduced pressure to recover distillate and residue fractions at a cut point of 343°C	1 mL to several litres	not applicable	2c
high resolution g.c. with f.i.d. of low boiling distillate or pentane solution	1 μL concentrated solution	qualitative method (See notes 1 & 2 below)	2d
The oil is extracted with petroleum spirit and the markers retained by passage through a Florisil column. They are then sequentially eluted with acetone and formic acid/acetone and identified by TLC	markers identified in 25 mg oil sample	50 ng quinizarin and 100 ng CI Solvent Red 24	2e
The saponification value is determined by completely saponifying the oil or fat with a known amount of potassium hydroxide, the excess of which is determined titrimetrically with 0.5 M HCl.	Not quoted	Not applicable	3a

Method number	Determinand	Type of sample
3b	Hydroxyl value (denotes the number of mg potassium hydroxide equivalent to the hydroxyl content in 1 g fat or oil). Acetyl value (denotes the number of mg potassium hydroxide equivalent to the acetic acid produced by the hydrolysis of 1 g of fat which has been acetylated).	Animal and vegetable oils
3c	Iodine value (denotes the amount of halogen, expressed as g iodine, which reacts with unsaturated groups in 100 g of fat under the conditions of the test).	The method describes the procedure for oils, fat and fatty acids and includes a modification for determining the iodine value of oils having conjugated double bonds such as tung oil and dehydrated castor oil.
3d	Acid value (denotes the number of mg potassium hydroxide required to neutralize 1 g of fat or oil).	Oils and fats
4	Classification of oils, fats, waxes and tars of unknown origin.	Oils, fats, waxes and tars
5	Sampling of oils, fats, waxes and tars in aqueous and solid systems, see note 3 below.	
6a	Those substances extracted by carbon tetrachloride (or 1,1,2 trichloro-trifluoroethane) under the conditions used in the method and which pass through a Florisil column of defined activity, and absorb infra-red radiation at the measuring wavelengths.	Natural waters including saline waters, drinking waters, sewage and industrial effluents.
6b	Those substances extracted by carbon tetrachloride under the conditions used in the method and which pass through a Florisil column of defined activity and which remain after evaporation at 105°C.	As for 6a.

Basis of method	Range of application	Limit of detection	
Acetylation of the hydroxyl groups with a known amount of acetic anhydride is measured titrimetrically (as acetic acid) using sodium hydroxide.	Not quoted	Not applicable	3b
The material under test is treated with an iodine monochloride solution. After addition of halogen, the excess of iodine monochloride is determined titrimetrically using thiosulphate solution.	Up to 200 Iodine value units	Not applicable	3c
The acid value is determined by titrating a solution of test sample to neutralization with 0.1 N potassium hydroxide solution.	Three methods are discussed: Method 1: is applicable to all fats other than oxidizable or polymerized fats, linseed oil, lanolin and wool fat. Method 2: is applicable to oxidizable or polymerized fats and to linseed oil, lanolin and wool fat. Method 3: is applicable to most animal and vegetable fats other than oxidizable or polymerized fats, linseed oil, lanolin and wool fat.	Not applicable	3d
A scheme of successive classification is used whereby the materials are classified according to their TLC and fluorescence properties.	Not quoted	Not applicable	4 5
The sample is extracted with carbon tetrachloride, the solvent extract is passed through a Florisil column and the eluate is analysed for hydrocarbon content by infra-red absorption of C-H stretching vibrations.	Using 2 mm cell up to 50 mg/kg. Using 10 mm cell up to 10 mg/kg. Using 40 mm cell up to 2.5 mg/kg.	0.06 mg/kg	6a
The sample is extracted with carbon tetrachloride, the solvent extract is passed through a Florisil column and the eluate is evaporated, dried at 105°C and weighed.	Typically up to 1000 mg/kg.	2.4 mg/kg	6b

Method number	Determinand	Type of sample
7	Those substances removed from industrial effluents and sewages after filtration and extraction by light petroleum spirit (40–60°C) and remaining after evaporation of the solvent.	Effluents, sewages and other waste waters.
8	Those substances extracted from sewage sludge by light petroleum (40–60°C) and remaining after evaporation of the solvent at 105°C.	Sewage sludge
9a	Hydrocarbons extracted by pentane under the conditions of the method which pass through a florisil column and are chromatographed and detected by GC-FID. Individual hydrocarbons and/or 'total detected hydrocarbons' are determined.	Water abstracted for potable supply and potable water.
9b	Volatile halogenated solvents	Drinking and river waters

Basis of method	Range of application	Limit of detection	
The sample is filtered through a GFC filter paper and the collected material is extracted into light petroleum spirit (40–60°C) in a soxhlet apparatus. The solvent is then evaporated off and the residue weighed.	Variable; the method is limited by blockage of the filter paper by the oil or fat. If the oil/fat is highly dispersed, acceptable filtration time might only be achieved with less than 100 ng of eventual extract.	3.6 mg/L	7
The sludge, acidified if required, is extracted with light petroleum (40°–60°C). The solvent is evaporated at 105°C and the residue weighed.	Up to 1 g of previously dried sludge	0.46%	8
Solvent extraction with pentane; removal of non-hydrocarbons with florisil; concentration; and separation and detection by GC-FID.	0.20 μg/L individual hydrocarbons	Total 5.7 μg/L. benzene 1.6 μg/L. toluene 0.1 μg/L. ethylbenzene 0.9 μg/L. (See note 4 below).	9a
Equilibration of the sample with its headspace vapour under controlled conditions. Injection of sample of the vapour into a gas chromatograph fitted with an electron capture detector.	The range of linearity depends on the detector and instrument in use. The range can be extended by injecting a smaller sample or by using the non-linear portion of the calibration curve.		9b

Compound	Linear range μg/L	Useable range μg/L	lod μg/L
1,1-dichloroethylene	0–15	0–80	0.6
1,1,1-trichloroethane	0–20	0–80	0.6
1,1,2-trichloroethane	0–15	0–50	2.0
tetrachloroethylene	0–10	0–20	1.6
1,1,1,2-tetrachloroethane	0–80	0–150	0.6
1,1,2,2-tetrachloroethane	0.50	0–100	0.5
carbon tetrachloride	0–5	0–15	0.1
trichloroethylene	0–20	0–80	1.0
chloroform	0–100	0–120+	0.7
bromodichloromethane	0–50	0–120+	1.1
dibromochloromethane	0–50	0–120+	0.5
bromoform	0–50	0–120+	0.7
pentachloroethane	0–10	0–40	0.8

Method number	Determinand	Type of sample
9c	Volatile halogenated solvents	Waters abstracted for potable supply and potable waters
10	Those substances extracted by pentane (or hexane) under the conditions used in the method and which fluoresce at the wavelengths selected (aromatic hydrocarbons).	Saline waters
11a	Methane and other gaseous hydrocarbons.	Ground, surface and potable waters.
11b	Methane and other gaseous hydrocarbons.	Ground, surface and potable waters.
12a	Six Polynuclear Aromatic Hydrocarbons (PAH) are measured, these are: Fluoranthene (FLU) Benzo(ghi)perylene (Bg hi Pe) Benzo(k)fluoranthene (BkF) Indeno (1, 2, 3-cd) pyrene (I 123cd P) Benzo (b) fluoranthene (BbF) Benzo (a) pyrene (BaP)	Potable, underground, reservoir, lake and river waters.
12b	6 Polynuclear Aromatic Hydrocarbons (PAH) are measured. (See 12a).	As for 12a.

Basis of method	Range of application	Limit of detection		
Extraction into petroleum ether (b.p. 30–40°C) followed by gas chromatography with electron capture detection.	Not quoted	1,1-dichloroethylene 1,1,1-trichloroethane 1,1,2-trichloroethane tetrachloroethylene 1,1,1,2-tetrachloroethane 1,1,2,2-tetrachloroethane carbon tetrachloride trichloroethylene chloroform bromodichloromethane dibromochloromethane bromoform pentachloroethane	0.03 (μg/L) 0.01 0.6 0.01 0.01 0.03 0.01 0.04 0.2 0.02 0.02 0.08 0.01	9a
The water is extracted with pentane and the solvent extract dried and analysed by fluorescence spectrometry.	0 to 18.5 μg/L	0.49 μg/L		10
Direct aqueous injection into a gas chromatograph fitted with a porous polymer packed column and a flame ionisation detector.	0–6 mg/L	0.13 mg/L		11a
Samples taken in a purpose made apparatus are vacuum degassed and analysed using a gas chromatograph fitted with a gas sampling valve, a packed column and a flame ionisation detector.	0–20 mg/L	0.4 vppm methane in headspace equivalent to 0.06 μg/L aqueous methane		11b
PAH are extracted from the sample by solvent extraction using cyclohexane. The concentrated extract is analysed using reversed-phase high-performance liquid chromatography with fluorimetric detection.	FLU up to approx 100 ng/L B ghi Pe up to approx 20 ng/L BkF up to approx 20 ng/L I 123cd P up to approx 20 ng/L BbF up to approx 20 ng/L BaP up to approx 20 ng/L	1.2 ng/L 1.7 ng/L 1.0 ng/L 1.1 ng/L 1.4 ng/L 1.3 ng/L		12a
Extraction of sample (1.8 litres) with cyclohexane, concentration of the extract and analysis using 2-dimensional thin layer chromatography. The PAH are estimated from the intensity of their fluorescence under ultraviolet illumination.	Up to 90 ng/L of each PAH	5 ng of each PAH, being the smallest amount visible on the standard plates. This corresponds to 2.8 ng/L with a 1.8 litre sample.		12b

Notes

Note 1. (For useful supplementary information see:

Indices for the identification of unknown substances by gas and other chromatography and related techniques 1988 in this series.

Note 2. (Compounds with higher boiling points than those detailed in these methods, such as paraffin waxes and normal alkanes with chain lengths greater than 30 carbon atoms may be analysed by extension of these techniques.

Note 3. This is not an analytical method but gives background information and outlines strategies to be used during sample collection.

Note 4. The procedure outlined in this method is intended to provide quantitative data on hydrocarbons at low concentrations which from experience appear to be important. 'Total Detected Hydrocarbons' may be estimated but one should be aware of the following problem. If the detection limit for individual hydrocarbons is X μg/L and for example, 10 hydrocarbons are present at 2 X μg/L then the total detected hydrocarbons would be 20 X μg/L. However, 40 hydrocarbons at X/2 μg/L (below the detection limit) would also total 20 μg/L but remain undetected.

The method will determine most of the hydrocarbon constituents in hydrocarbon materials such as petrol, paraffin, diesel oil, gas oil, petroleum solvents etc. Those not covered would be hydrocarbons boiling outside a range of about 60–340°C.

The method is mainly applicable to clean waters, such as water abstracted for potable supply and potable water.

Alternative Analytical methods

Analysis of Waxes

(i) IP/372/85

This is a gas chromatographic method which uses a stainless steel column 1.2 m by 3 mm o.d. (i.d. not less than 2 mm)—5% silicone gum rubber OV12 on Chromasorb W (HMDS). Flow 18 to 30 mL/min of Helium or Nitrogen. Programme 4°C to 6°C/min over the range 120 to 320°C. Injection Temp 375 to 450°C, with detector the same. The reference sample contains n-C20, C24, C28, C32, C36, C40, with HCs detected in the range C18 to C40.

(ii) ASTM methods

Although there is not a current ASTM standard, a study group is developing a method. They favour wide bore, thin film bonded phase fused silica capillary columns again with FID detection. The column is 30 m by 0.53 mm i.d. The liquid phase is SPB-1 Crosslinked dimethyl polysiloxane, 0.25 mm thick. The Carrier gas is He at 20 p.s.i and flow of 209 ml/min. The programme range is 75° to 300°C, at a rate of 25°C/min. Good resolutions of components of standard mixtures up to C44 were obtained. Unknowns up to C46 or with elevated temps up to 340°C up to C60 can be successfully analysed with good resolution. A polywax was analysed up to C70 in 44 mins.

(iii) Other Chromatographic work

At the Petro Analysis 87 Symposium A. Barker of Campbel gave a paper on trends in Wax analysis. He had modified the IP method, running up to 375 or even 400°C for a short time. He reached a recognisable C70 on a microcrystalline wax (over the unresolved hump typical of m.c.s.).

With capillary columns of 25 m by 0.33 with DB-1 at 0.2 thickness and programmed to 370 deg C he obtained better resolution above C35.

Using 15 m by 0.25 mm of 0.1 μm film thickness to 400°C he could separate C. Nos up to C90 (high purity Oxygen free gases were needed to preserve the columns). (see fig 5).

More progress may now be made with Super Critical Fluid Chromatography (SFC) using compressed carbon dioxide as carrier and short narrow capillaries coated with OV phases. With SFC a Fischer Tropsch Wax with components up to C100 was separated (Figure 6).

Standard wax blend capillary column chromatograms

Figure 4

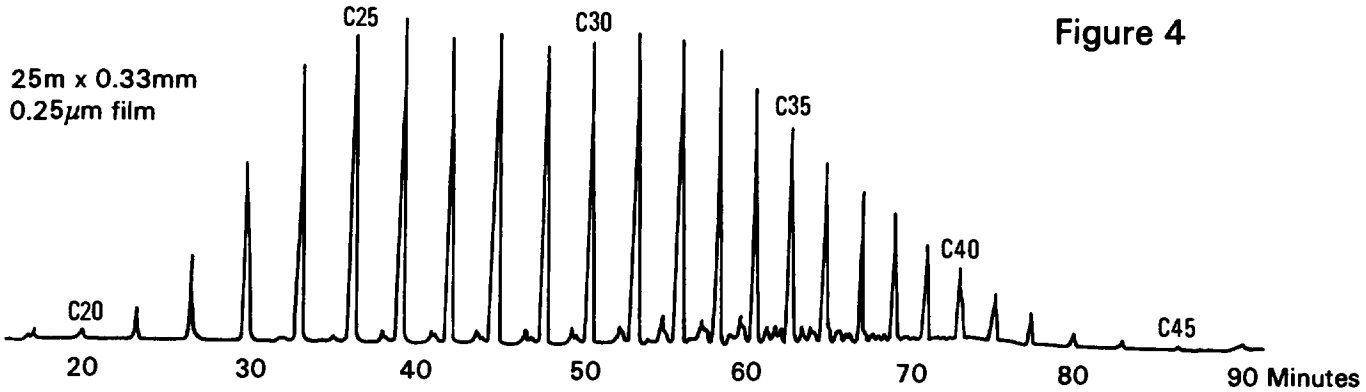
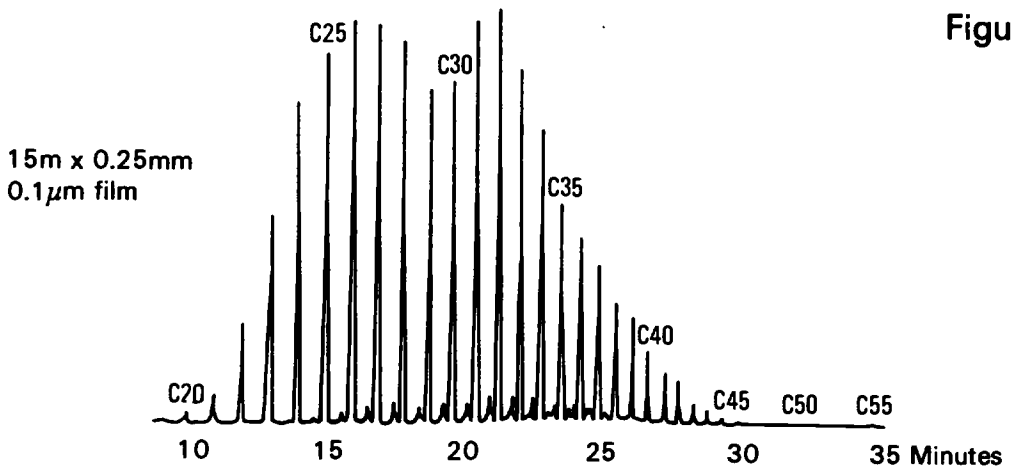
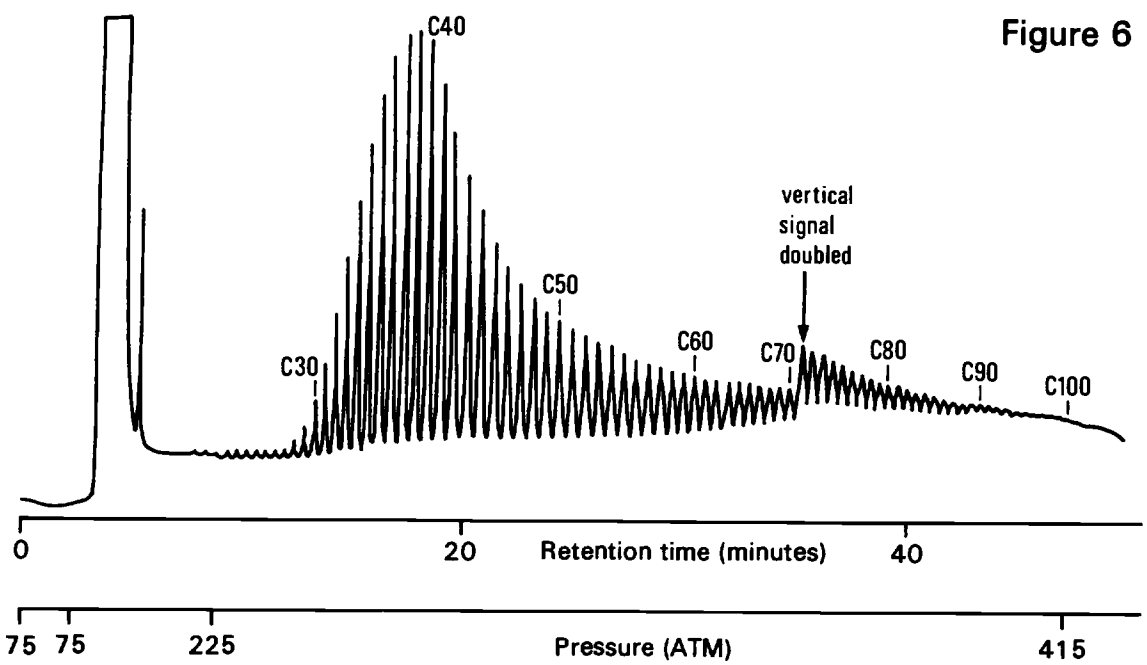


Figure 5



SCF/FID chromatogram of a Fischer-Tropsch wax

Figure 6



Analysis for Gases

(iv) Infra Red Absorption

Commercially available IR absorption instruments, capable of remote operation if necessary, using long path length calls are now available for methane, ethylene, acetylene and propane (and some other gases*) at down to 10 ppm in air (or head spaces). Tuneable Laser diodes are used as sources so that the source corresponds to a precise absorption peak frequency for the determinand. (University of Manchester Wolfson Laser Unit Dept. of Physics information).

Many other references are to hand but the above summarises the most useful methods which are in current practice.

*HCl, CO_2, NH_3, NO_2.

General

Linear Temperature Programmed Retention Indices can be used for the tentative identification of many substances including non gaseous hydrocarbons. See Ref 5 of the next Chapter.

Analysis for Hydrocarbons with over Thirty Carbon Atoms per Molecule—a Note

Gas chromatographic methods which extend to higher carbon number alkanes, nC_{35} or greater, have been developed by many workers for the determination of oil in Water. Generally these methods consist of two stages, a concentration step followed by capillary gas chromatography of the concentrate. Many workers would also add as a preliminary step, separation of the particulate material (of size > 0.5–1 micron) from the sample by membrane filtration.

Liquid—liquid extraction procedures have been used for concentration of oil in water samples by several workers (1–3); the overall concentration factor they achieved, after evaporation of the extract, ranging from $\times 200$ to $\times 3{,}300$. Some workers (3,4) have also used resin methods, particularly those based on XAD-2, for concentration of oil in aqueous samples.

Gas chromatographic determination of the oil content of the concentrates has been carried out by temperature programmed capillary gas chromatography using a flame ionisation detector (1–4). The final column temperature which has been employed is normally greater than 270°C to ensure elution of the higher chain length alkanes.

The detection limits obtained by these methods depend principally on the overall concentration achieved. Typically, a concentration factor of $\times 500$ would produce a detection limit of ~ 1 μg/L in the original sample for each of the n-alkanes covered by the method. However, it should be noted that the concentration procedures listed in this appendix could lead to loss of some of the more volatile hydrocarbons eg nC_{10} and below.

It is suggested that analysts needing to determine higher hydrocarbons than about C_{30} should analyse by a suitable method (or methods) to identify individual lower hydrocarbons, followed by a procedure based on this note and if necessary sum the various hydrocarbons found. This ensures that a falsely high value is not obtained by counting the same material twice. It should be noted that the Linear Temperature Programmed Retention Index curve for hydrocarbons on high temperature capillary columns can with care be extended to at least C_{80} (5).

See also the Analyses of Waxes Section in the Review above.

References

(1) Alexander R; Cumbers M; Kagi R; Offer M and Taylor R. Petroleum Contamination of Cockburn Sound, Western Australia in Chemistry and Analysis of Hydrocarbons in the Environment. Gordon and Breach. 1983 pp273–297

(2) Ducreux J; Boulet R; Petroff N and Roussel J C. Comparison de Differentes Methodes Analytiques Appliquees au Dosage des Hydrocarbures Dissous dans L'eau a L'etat de Traces. ibid pp89–103

(3) Ho R; Marty J-C and Saliot A. Hydrocarbons in the Western Mediterranean Sea. Ibid pp235–252

(4) Burns K A and Villeneuve J-P. Dissolved and Particulate Hydrocarbons in Water from a Spring Sampling of the Var River Estuary (S. France). Ibid pp263–271

(5) Indices for the Identification of Unknown Organic Substances by Gas and Other Chromatography and Related Techniques 1988. HMSO (in this series).

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