The Determination of Hydrocarbon Oils in Waters by Solvent Extraction, Infra Red Absorption and Gravimetry 1983

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £2.75 net

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Methods for the Examination of Waters and Associated Materials

This booklet contains two methods one using Infra Red Absorbance the other Gravimetry, both Tentative

Contents

Some methods are very sensitive to minor physical and chemical variations in the quality of the materials and apparatus used. Hence this method mentions actual materials and instruments used for the evaluation tests. This in no way endorses these materials and instruments as superior. Equivalent materials and instruments are acceptable, though it must be understood that the performance characteristics may be different. It is left to the senior supervising analyst to evaluate and choose from the appropriate brands and makes available.

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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 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.

First published 1984

ISBN 0 11 751728 3

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 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 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 seven 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
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.

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

31 October 1983

The Determination of Hydrocarbon Oil in Waters by Solvent Extraction and either Infra Red Absorption or Gravimetry

Introduction

01 Because of the wide range of materials which could come under the broad definition of oil and grease (historical description) no one analytical method can be expected to determine all the substances so described. The analytical methods in this document are for:

> Materials extractable by carbon tetrachloride (or 1, 1, 2 — trichloro, 1, 2, 2 — trifluoro ethane) under defined conditions and which pass through a Florisil column of a defined activity. If the gravimetric method is used, there will also be a minimum boiling point limitation on the materials.

The methods are non specific covering a wide range of substances. This definition will also include some substituted hydrocarbons. (See Sections A1, A3 and A11.)

Most natural oils and fats will be retained on the Florisil column. These can be subsequently removed by a suitable solvent or mixed solvent and can be quantitatively determined. (See another publication in this series.)

02 Method A involves the use of an infra-red spectrophotometer while Method B although using an identical extraction technique relies on weighing.

03 Although the infra-red procedure has been well evaluated and bias results produced for a wide range of hydrocarbon oils, it must be stated that the number of individual compounds in any one "oil" could vary between many hundreds and just a few and in these latter instances there is the possibility of bias results outside those given in A1.9. Where the exact character of an oil is known the source material may be used as a reference for the measurement of concentration in a sample, see Section A11.

04 Emulsifying materials have not been considered as possible interferants for two reasons. Firstly, the substances determined are defined within the methodology, and secondly there is a lack of well documented evidence of the conditions under which emulsified oil can be extracted. It is hoped as these methods gain acceptance that work can be carried out to investigate the effect of different emulsifying agents with different types of hydrocarbon oils.

05 These methods form part of a continuing series which, when complete can be used as part of a general co-ordinated scheme of analysis. (See another publication in this series.) Variations of them may be used to measure related determinand concentrations. Omission of hydrochloric acid as a sample preservative from the Analytical Procedures will yield the hydrocarbon oil fraction of the unacidified carbon tetrachloride (or 1, 1, 2 trichloro-, 1, 2, 2 trifluoro ethane) extractable material not retained by Florisil. The omission of Florisil from Method B will give the total acidified (or unacidified) carbon tetrachloride (or 1, 1, 2 trichloro-, 1, 2, 2 — trifluoro ethane) extractable material.

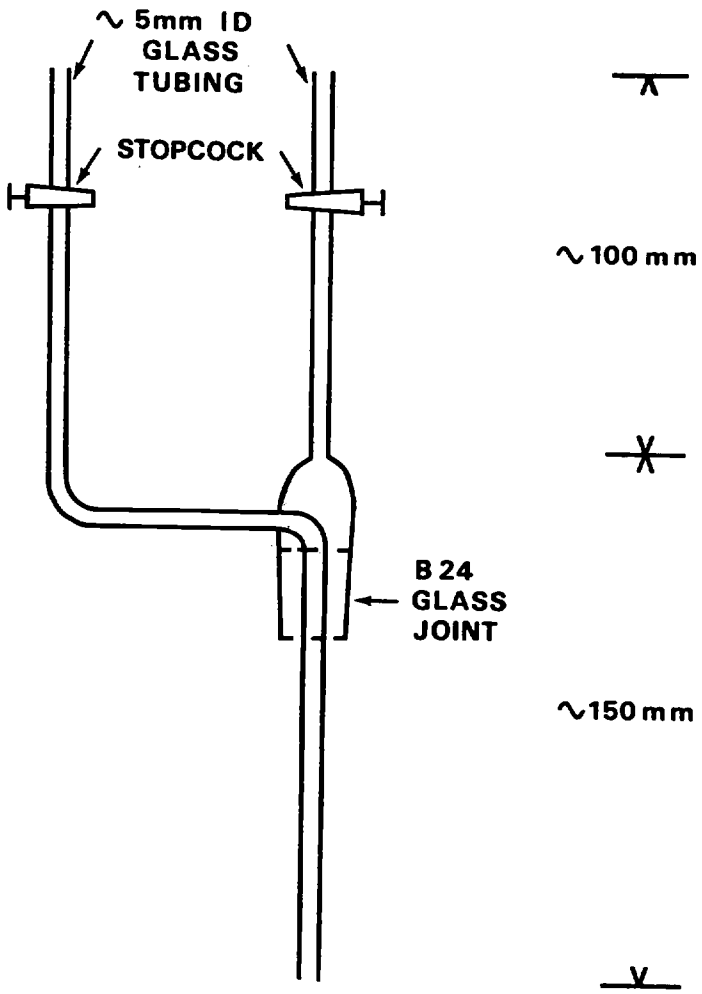

Figure 1

Method A: Determination of hydrocarbon oil in water by infra-red absorption

A1.1 Performance Characteristics of the Method

A1.1	Substance determined	Those substances extracted by carbon tetrachloride (or 1,1,2 trichloro-, 1,2,2 trifluoro, ethane (TTE)) 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.
A1.2	Type of Sample	Natural waters including saline waters, drinking waters, sewage and industrial effluents.
A1.3	Basis of Method	The water 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.
A1.4	Range of Application	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
A1.5	Calibration Coefficients (a)	Dependent on cell characteristics and possibly on (see Table IV) the instrument used.
A1.6	Standard Deviation (a)(b) (See also Section A11)	See table below
A1.7	Limit of Detection (a)(b)	0.06 mg/kg (with 11 degrees of freedom) (This figure obtained using a Perkin Elmer 683 infra red spectrophotometer.)
A1.8	Sensitivity (a)(b)	200 mg/l n-hexadecane in CCl_4 gives an absorbance of 1.044 at 2930 cm^{-1} 200 mg/l pristane in CCl_4 gives an absorbance of 0.508 at 2960 cm^{-1} 200 mg/l toluene in CCl_4 gives an absorbance of 0.117 at 3030 cm^{-1} (These figures may be instrument dependent and are for a Perkin Elmer 683 model.)

A1.6 Standard Deviation (a)(b) (See also Section A11)

Synthetic Oil Concentrations mg/kg	Standard Deviation within-batch mg/kg	Degrees of Freedom
1	0.08	6
4	0.11	6
20	0.62	6

A1.9	Bias (b)	Up to ± 15% depending on type of oil. Tables I and II give a range of oils evaluated (see Section A0.3). If the actual oil is available procedures outlined in Section A11 can be carried out and any calibration bias eliminated (see also A12).
A1.10	Interference	Any material passing through the Florisil column absorbing at the recommended wavelengths, and not a hydrocarbon oil or a compound for which determination is not required by this method.
A1.11	Time Required for Analysis	One sample could be completed in 1 hour (all operator time), after the method is in routine use; for multiple analysis, this could be reduced to 0.5 hr or 0.3 hr depending on laboratory facilities.

(a) Section A1.5 and A1.8 are based on standard solutions of n-hexadecane, pristane and toluene in carbon tetrachloride (see A5.10). Sections A1.6 and A1.7 are based on a mixture of these compounds in the ratio 5:3:1.

(b) Data produced in Sections A1.6, A1.9 and A12 were obtained from the North West Water Authority, Rivers Division, by P J Whittle, W A McCrum and M W Horne.

A2 Principle

The hydrocarbon oils are extracted by liquid — liquid extraction into carbon tetrachloride (or TTE). The extract is passed through a Florisil column to remove non-hydrocarbon compounds.

The concentration of hydrocarbon oil is calculated after measuring the infra-red absorbances of the eluate at 2930 cm^{-1} (C-H stretch in CH_2 groups), 2960 cm^{-1} (C-H stretch in CH_3 groups) and 3030 cm^{-1} (C-H stretch in aromatic rings).

A3 Interferences

For most practical purpose the only compounds interfering would be some halogenated hydrocarbons eg. trichloro-ethane. In specific instances (eg. effluents containing other organic compounds with polarity characteristics similar to hydrocarbons) more detailed investigation may be necessary.

A4 Hazards

The procedure described uses carbon tetrachloride which is toxic. Avoid inhalation, skin contact and ingestion. Carbon tetrachloride can be an anaesthetic and repeated heavy exposure can cause liver damage. This solvent may be replaced by 1,1,2 trichloro-, 1,2,2 trifluoro-ethane which is less hazardous. Wear gloves and work in a well ventilated room or under an efficient fumehood (see also Section A12).

A5 Reagents

All reagents must be of sufficient purity that procedural blanks give acceptable low infra-red absorbances at the measuring wavelengths. Reagents may become contaminated by contact with air and with materials, particularly plastics. Therefore, storage should be in tightly sealed all-glass containers or other vessels found to be suitable.

A5.1 Carbon tetrachloride (A R grade, is usually sufficient) (or 1,1,2 trichloro-, 1,2,2 trifluoro-ethane (TTE)). This may be checked for impurities (see A3.3).

A5.2 Florisil 30/60 mesh — Heat at 500°C ± 20°C in a silica dish in a muffle furnace for at least 2 hours. Cool to 200°C in the furnace and then to ambient temperature in a desiccator where it may be stored for a month.

A5.3 Prepared Florisil — To a suitable weight of dry Florisil in an-all glass container add 6% ± 0.5% W/W water, stopper tightly and shake for several minutes. Allow to stand overnight. Prepare freshly each week.

A5.4 Concentrated Hydrochloric Acid d_{20} 1.18 — Analytical reagent grade.

A5.5 Sodium Chloride — Most grades are suitable.

A5.6 **Magnesium Sulphate** — Analytical reagent grade, $MgSO_4 H_2O$. Heat to 500°C ± 20°C for 4 hours. Cool to 200°C in furnace then to ambient temperature in a desiccator.

A5.7 **Toluene** — Analytical reagent grade.

A5.8 **n-Hexadecane** —Analytical reagent grade.

A5.9 **Pristane** — 2,6,10,14-Tetramethyl pentadecane — Analytical reagent grade.

A5.10 **Standard Solutions:**

Individual standards of n-hexadecane, pristane and toluene may be made up to give solutions in carbon tetrachloride or 1,1,2 trichloro-, 1,2,2 trifluoro-ethane which produce appropriate peaks within the linear absorbance range of the instrument being used (typically in the range 100–200 mg/l for 10 mm cuvettes).

These solutions may be prepared by making up stock solutions by weighing, dissolving in carbon tetrachloride and dilution as required.

A5.11 **Synthetic standard** for method evaluation. Prepare a mixture of the toluene, pristane and n-hexadecane in the ratio 1:3:5 by volume.

A6 Apparatus

A6.1 **Solvent removal device** (see fig. 1).

A6.2 **Teflon B24 bottle top**, converts standard glass Winchester screw thread into a B24 socket for use with solvent removal device. (Available from Jencons Scientific Limited.)

A6.3.1 **Glass Columns — Glass chromatography column** approximately 100 mm long × 10 mm I D (Quickfit CR 12/10 suitable).

A6.3.2 **Preparation.** Fill glass column (A6.3.1) to within 2 cm of the top with carbon tetrachloride. Add prepared Florisil with gentle tapping until it is packed to a depth of about 3 cm. Then add magnesium sulphate until the column is packed for approximately a further 1 cm.

A6.3.3 **Preparation.** Fill a glass column (A6.3.1) to a depth of 8 cm with the prepared Florisil using gentle tapping to settle.

A6.4 **Bottle Rolling Machine.** Any rolling device capable of producing about 60 rev/min bottle speed.

A6.5 **An infra-red spectrophotometer with I R grade silica cells** of 2 mm, 10 mm and 40 mm pathlength.

A6.6 **Standard laboratory glassware.**

A7 Sample Collection and Preservation

Representative sampling of oil-water mixtures is well known to be difficult and reference should be made to a general text on sampling (see other publications in this series (3)). However, it is reasonable to comment that the ideal situation would be piped waters or pumped sampling loops tapped directly into the sampling bottle and modifications of this should be evaluated critically.

If analysis is not carried out within 24 hours the sample should be acidified to pH2 stored in a refrigerator at 4°C, or CCl_4 added as 2.5% of the sample volume. Wherever possible a note should be made of the weight or volume of preservative added (see note (a) Analytical Procedure).

A8 Analytical Procedure

Step	Procedure	Notes
A8.1	**Extraction**	
A8.1.1	Weigh the sample bottle plus sample liquid (W_1 g) (note a)	(a) It is usual to analyse 1 litre of sample and so its weight (W_1–W_2, see also A8.1.6) is obtained ± 1 g; this would be proportionately smaller for smaller volumes. Sometimes it is necessary to analyse a portion of a much larger sample volume; under these circumstances the whole sample should be shaken vigorously and the 1 litre portion transferred to a bottle suitable to this procedure. However wherever possible the whole sample should be analysed to minimise errors caused by oil adhering to the bottle.
A8.1.2	To the sample liquid add approx. for each litre of liquid (i) 40 ± 1 g of sodium chloride (ii) 2 ± 0.1 ml of conc. H Cl Then add 25.0 ± 0.1 ml of carbon tetrachloride (see notes b and c)	(b) If acid has been added as a preservative further additions will not be required. Similarly if CCl_4 has been added further additions will be unnecessary. (c) For very alkaline samples it may be necessary to add more acid. If the pH of the sample is measured do not use an electrode on the portion to be analysed because oil may adhere and will have to be removed with consequent analytical problems. 1,1,2 trichloro-, 1,2,2 trifluoro-ethane may be used in most instances, instead of carbon tetrachloride as an extractant (see also Section A12); the same conditions apply.
A8.1.3	Replace the bottle screw cap with the teflon B24 bottle cap and B24 glass stopper. Shake vigorously for one minute and roll for 30 minutes (note d)	(d) Any oil adhering to the bottle cap should be washed into the bottle with an aliquot of the carbon tetrachloride used for extraction.
A8.1.4	Decant most of the aqueous layer and run off the carbon tetrachloride into conveniently small glass beaker by means of the solvent removal device.	
A8.1.5	Dry the extract in the beaker by the addition of sufficient magnesium sulphate (note e)	(e) Alternatively plug a glass filter funnel with glass wool, add magnesium sulphate into the funnel and decant the extract through the funnel.
A8.1.6	Weigh the empty sample bottle (W_2 g)	
A8.2	**Clean-up procedure**	
A8.2.1	Prepare a Florisil column as described in A6.3.2. Run off surplus carbon tetrachloride.	
A8.2.2	Wash the column through with 10 ml ± 1 ml of extract, discard and then run enough sample through the column to fill the infra-red cell (see notes (f) and (g)	(f) If a dilution is required this may be carried out before clean-up. The "uncleaned" extract may be scanned (as in A8.3.1) to see if the absorbances are outside the linear range of the instrument for the cell being used. If so a suitable dilution and/or a different cell path length is required. (g) Care should be taken not to overload the column. The capacity is around 30 mg of fatty material.

Step	Procedure	Notes
A8.3	**Infra-red determination**	
A8.3.1	Using a suitable cell path length scan the infra-red absorbance of the extract or diluted extract after clean-up, between 2400 cm^{-1} and 3400 cm^{-1}. Measure the absorbances of the peaks at 2930 cm^{-1}, 2960 cm^{-1} and 3030 cm^{-1}. Use carbon tetrachloride in the reference cell from the same batch as that used for extraction and dilution (notes (f), (h), (i) and (j)).	(h) If the oil extracted does not have a very high aromatic content no peak may be resolved at 3030 cm^{-1}. In this case simply measure the absorbance at this point. (i) Carbon tetrachloride used in the reference cell must be purified by passage through Florisil steps A8.2.1 should be used for this. (j) It may be necessary to dilute the cleaned extract to bring the absorbance to within the linear range of the instrument (if this has not been done already under note e).
A8.4	**Calculation**	
	The concentration of oil in an original aqueous sample may be calculated from the equation.	
	$C = \left[x\ A_{2930} + y\ A_{2960} + z\left(A_{3030} - \frac{A_{2930}}{F}\right)\right] \frac{V.D.10}{(W_1 - W_2)L}$	
	Where C = conc. of oil in original sample in mg/kg; x, y and z are the calibration coefficients described in Section A10. F is the correction factor described in Section A10 (note m). A_{2930}, A_{2960} and A_{3030} are the appropriate absorbances. V is the volume of carbon tetrachloride used for extraction in ml. W_2 and W_1 are the weights of the sample bottle and sample bottle plus sample respectively (note k). D is the dilution factor. L is the cell path length in mm. (note l)	(k) Allowance must be made for weight of added preservatives. (l) The equation assumes that the calibration for x, y and z was carried out using 10 mm cells. (m) For most practical purpose mg/kg is equivalent to mg/l.

A9 Blanks

The blank from the carbon tetrachloride is eliminated by using the same batch of solvent in the reference cell making any corrections unnecessary, the path lengths of the cells used for blank and sample should be sufficiently similar to permit this balancing to occur. Reagent blanks at these levels of oil determination are insignificant and do not need to be incorporated in any calculations, but complete procedural blanks should be done to ensure contamination is not occurring in the sampling and extraction steps. If significant blanks are obtained procedures must be investigated and steps taken to eliminate them.

A10 Preparation of Calibration Coefficients

Procedure	Notes
Scan the infra-red spectra of the standard solutions of n-hexadecane, pristane and toluene (A5.10) in 10 mm cells between 2400 cm^{-1} and 3400 cm^{-1} to measure the absorbances at 2930 cm^{-1}, 2960 cm^{-1} and 3030 cm^{-1} using a common base-line drawn between 3,300 cm^{-1} and 2600 cm^{-1}.	

Procedure	Notes
For each compound the absorbances are submitted in the general equation $c = x.A_{2930} + y.A_{2960} + z\left(A_{3030} - \frac{A_{2930}}{F}\right)$ to give three simultaneous equations where c = conc. in mg/l of the compounds in the solvent. x, y and z are the coefficients (note a) related to the absorptivities of the C-H stretching modes, F is the correction factor for the effects of the aliphatic groups on the aromatic group, (note b) and A_{2930}, A_{2960} and A_{3030} are the absorbances measured at 2930 cm^{-1}, 2960 cm^{-1} and 3030 cm^{-1} respectively in the three spectra.	(a) Once the coefficients x, y and z are determined for a particular instrument under a particular set of conditions, they should remain stable and should need to be checked only occasionally. Some typical values are given in Table IV.
Since the aromatic concentrations of n-hexadecane and pristane are zero, calculate x and y from the equations obtained for n-hexadecane and pristane (note c).	(b) In practice, F is calculated from the ratio of the absorbances at 2930 cm^{-1} and 3030 cm^{-1} for n-hexadecane.
Calculate F from $\frac{A_{2930}}{A_{3030}}$ for n-hexadecane. Substitute x, y and F into the equation for toluene and determine z. A worked example is given in Section A13.	(c) This is true for n-hexadecane (from the definition of F), but is an assumption for pristane.
Scan the infra-red spectrum of the synthetic mixture (A.5.11) between 2400 cm^{-1} and 3400 cm^{-1}. Measure the absorption at 2930 cm^{-1}, 2960 cm^{-1} and 3030 cm^{-1} and substitute the values of x, y, z and F determined to evaluate the accuracy of the coefficients for the synthetic mixture. If the calibration bias of real oil solutions is required follow the procedures described in Section A11.	

A11 Preparation of Actual Oil Standards for Calibration Bias Correction or Method Performance

A11.1 Low Viscosity Oils

Pass 10 ml of the oil through a column prepared as in A6.3.3. Reject the first 1 ml and collect the next ml of eluate oil. Using this oil, standards can be prepared in CCl_4 using a syringe. If the S.G. is known the weight may be calculated directly otherwise the syringe can be weighed before and after addition.

A11.2 High Viscosity Oils

Mix 1 ml of oil with 5 ml of redistilled pentane and pass this mixture through a column prepared as in A6.3.3, rejecting the first 1 ml of eluate. Wash through with a further 10 ml of pentane and collect all eluate in a 25 ml beaker. Remove pentane by evaporating at 50°C with a gentle stream of air directed onto surface. Using this prepared oil, standards can be prepared in CCl_4 using a syringe weighed before and after additions.

A11.3 For extraction performance bias experiments appropriate quantities of samples prepared in this way should be injected directly into the sample bottle, using either the weight of the syringe before and after or the S.G. to obtain specific weights. On no account must stock oil/water mixtures be prepared.

A11.4 It should be noted that bias experiments performed with oil standards prepared in this way will give only correction for the calibration coefficients and extraction efficiency and will not correct for material present in the actual oil but retained by Florisil. (See Table I.)

A11.5 Use of source material

If the analyst wishes to quantify an actual source oil in total by this method, (ie. take into account any non hydrocarbon additives etc.) then the initial Florisil step should be omitted and the source oil quantitatively injected into a sample bottle using the alternative techniques outlined in Section A11.1.

Table I Calibration bias results (obtained using coefficients obtained from reference solution)

The following results show mean recoveries, ie. (mean calculated concentration ÷ true concentration × 100) (ref. 2)

Oil Standard*	% Recovery with carbon tetrachloride	% Recovery with TTE
White spirit	108.1 (2.28 S.D.)	110.5
Premium kerosene	106.9	—
Regular kerosene	108.0	—
Petrol, 3-star	102.2	98.0
Gas oil 1	95.3	101.0
Gas oil 2	96.1	—
Lube oil, 20W	88.9	—
Lube oil, 20W/50	87.7 (0.64 S.D.)	89.7
Residual fuel oil	89.3	—
North Sea crude	107.6	—
Light Nigerian crude	101.1	—
Kuwait crude	101.0	—
Range	87.7 – 108.1 (6 replicates)	—
Range, %	20.4	
Mean	99.4	

* 160 ± 10% mg/l

These figures were obtained using the methodology given in Section A11.1 and A11.4. The recovery was calculated from measured concentration and prepared concentration. The standard deviations for the percentage recoveries of the standards examined ranged from 2.28 for white spirit to 0.64 for 20W/50 lube oil giving respective maximum possible biases of + 10.0% and – 12.8%.

Table II Extraction recovery results

The following results show mean recoveries of gas oil at different concentrations in a potable water. (Mean of seven replicates.)

Conc. mg/kg	% Recovery	Relative Standard Deviation
1.0	108	8.4
4.0	96	2.8
20.0	94	3.1

The solutions were prepared by addition of solvent solutions of gas oil to water. The extracted oil and oil itself were then compared through the whole procedure, calibration bias was eliminated because it would cancel out in the recovery calculation.

A12 Use of 1,1,2 Trichloro-1,2,2 Trifluoro-Ethane

It is recognised that because of the suspected hazardous properties of carbon tetrachloride, some laboratories no longer use this chemical as an extractant and only use 1,1,2 trichloro-, 1,2,2, trifluoro-ethane (TTE) as a replacement. Carbon tetrachloride is the preferred solvent in this method because TTE gives poorer recoveries and forms emulsions which are difficult to break. Tables III and IV give some performance data for the method when TTE is substituted for carbon tetrachloride. Equivalent carbon tetrachloride data are given.

Table III Extraction recoveries of gas oil using carbon tetrachloride and 1,1,2 trichloro-, 1,2,2 trifluoro-ethane

Hydrocarbon	Concentration, mg/l in carbon tetrachloride extract			Concentration, mg/l in TTE extract		
	Mean[a]	S.D.	Recovery[b] %	Mean[a]	S.D.	Recovery[b] %
5 μl standard (see Section A5.11)	150	2.36	—	169.6	6.48	
1.25 μl gas oil	40.6	3.40	108.3	34.8	4.92	82.1
5 μl gas oil	144	3.96	96.0	146	6.72	86.1
25 μl gas oil	703	22.0	93.7	744	25.0	87.8

[a] Seven replicates through whole procedure

[b] The recoveries shown are based on the measured concentration of the standard solution and thus eliminate calibration bias.

Table IV Typical calibration coefficients

Factor	Solvent	
	Carbon tetrachloride	TTE
x	177.4	132.8
y	299.4	183.4
z	1960	1255
F	34.6	31.2

A13 Worked Example for the Derivation of Calibration Coefficients (Ref. 1)

A13.1 Absorbance for 160 mgl^{-1} solutions of the compounds in carbon tetrachloride, 10 mm cells, mean of 10 measurement

	A_{2930}	A_{2960}	A_{3030}
Hexadecane	0.5225	0.2249	0.0151
Pristane	0.3537	0.3249	0.0137
Toluene	0.0407	0.0286	0.0748

$$F = \frac{A_{2930}}{A_{3030}} \text{ for hexadecane } = \frac{0.5225}{0.0151} = 34.6$$

A13.2 The factors x, y and z are calculated from the solution of 3 simultaneous equations of the type

$$c = x\,A_{2930} + y\,A_{2960} + z\left(A_{3030} - \frac{A_{2930}}{F}\right)$$

$$\text{for hexadecane } 160 = x\,0.5225 + y\,0.2249 + z\left(0.0151 - \frac{0.5225}{F}\right) \quad (1)$$

$$\text{pristane} \quad 160 = x\,0.3537 + y\,0.3249 + z\left(0.0137 - \frac{0.3537}{F}\right) \quad (2)$$

$$\text{toluene} \quad 160 = x\,0.0407 + y\,0.0286 + z\left(0.0748 - \frac{0.0407}{F}\right) \quad (3)$$

A13.3 For pure hexadecane and pristane the aromatic CH absorption should be zero, the small recorded measurements at 3030 cm^{-1} being due to the shoulder of the CH_2 and CH_3 peaks.

For hexadecane the term $\left(A_{3030} - \frac{A_{2930}}{F}\right)$ is zero

and it is assumed that the term for pristane also approximates to zero. Equations (1) and (2) can then be solved to give

$x = 177.4$; $y = 299.4$, substituting the value for x and y

in equation (3) $z = 1960$

A14 References

(1) Whittle P. J., McCrum W. A. and Horne M. W. Infra-red determination of petroleum oil: New approaches to the calculation. *Analyst*, 1980, **105**, 697–684.

(2) McCrum W. A. and Whittle P. J. Infra-red determination of petroleum oil: II Extraction from water and removal of interferences. *Analyst*, 1982, **107**, 1081–1085.

(3)(a) *General Principles of Sampling and Accuracy of Results 1980.* HMSO, London.

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

(c) *Sampling of Rivers and Streams 1983.* HMSO, London.

Method B: Determination of hydrocarbon oil in water by gravimetry

B1 Performance Characteristics of the Method

B1.1	Substance determined	Those substances extracted by carbon tetrachloride (or TTE) under the conditions used in the method and which pass through a Florisil column of defined activity and remain after evaporation at 105°C.
B1.2	Type of Sample	Natural waters including saline waters, sewage and industrial effluents.
B1.3	Basis of Method	The water is extracted with carbon tetrachloride (or TTE) the solvent extract is passed through a Florisil column and the eluate is evaporated, dried at 105°C and weighed.
B1.4	Range of Application	Typically up to 1000 mg/kg

B1.5 Standard Deviation

	S_W mg/kg	S_B mg/kg	S_T mg/kg	RS_T%
0	0.43	—	—	—
57.5 mg/kg lube oil	5.8	NS	8.7	18.5
497 mg/kg lube oil	28.9	NS	34.6	7.8
56.6 mg/kg diesel oil	1.4	4.3	4.5	12.4
502 mg/kg diesel oil	11.2	NS	12.4	2.8

(9 degrees of freedom)

NS not significant

B1.6	Limit of Detection	2.4 mg/kg (9 degrees of freedom)

B1.7 Bias

	Mean % Recovery	90% nonf. Limits (%)	Worst Possible % Mean Recovery
57.5 mg/kg lube oil	81.52	± 11.55	69.97
497 mg/kg lube oil	89.69	± 4.67	85.02
56.6 mg/kg diesel oil	68.46	± 7.41	61.05
502 mg/kg diesel oil	87.96	± 1.57	86.39

B1.8	Interference	Any material passing through the Florisil column which is not a hydrocarbon oil, or a compound for which determination is not required by this method.

B1.9	Time Required for Analysis	In pairs, 1½ hrs analytical time 1 hr operator time.

These results were obtained by R. Leach and D. Partridge of the Cambridge College of Art and Technology under contract to the DOE.

B2 Principle

The hydrocarbon oils are extracted by liquid — liquid extraction into carbon tetrachloride. The extract is passed through a Florisil column to remove non-hydrocarbon compounds.

The solvent is removed from the eluate using firstly a rotary evaporator and then a steam bath. The residue is dried at 105°C and then weighed.

B3 Interferences

For most practical purposes the only compounds interfering would be halogenated hydrocarbons. In specific instances (eg. effluents containing other organic compounds or extractable material) more detailed investigation may be necessary.

B4 Hazards

The procedure described uses carbon tetrachloride which is toxic. Avoid inhalation, skin contact and ingestion. Carbon tetrachloride can be an anaesthetic and repeated heavy exposure can cause liver damage. This solvent can be replaced by 1,1,2 trichloro-, 1,2,2 trifluoro-ethane which is less hazardous. (See Section A12.)

Wear gloves and work in a well ventilated atmosphere.

B5 Reagents

Reagents may become contaminated by contact with air and with materials, particularly plastic. Therefore, storage should be in tightly sealed all-glass containers or other vessels found to be suitable.

B5.1 Carbon tetrachloride A.R. grade (or 1,1,2, trichloro-, 1,2,2 trifluoro-ethane).

B5.2 Florisil 30/60 mesh — Heat at 500°C ± 20°C in a silica dish in a muffle furnace for at least 2 hours. Cool to 200°C in the furnace and then to ambient temperature in a desiccator where it may be stored for a month.

B5.3 Prepared Florisil — To a suitable weight of dry Florisil in an all-glass container add 6% ± 0.5% W/W water, stopper tightly and shake for a few minutes. Prepare daily.

B5.4 Concentrated Hydrochloric Acid d_{20} 1.18 — Analytical reagent grade.

B5.5 Sodium Chloride — Most grades suitable.

B5.6 Magnesium Sulphate — Analytical reagent grade. $MgSO_4 H_2O$. Heat to 500°C ± 20°C for 4 hours. Cool to 200°C in furnace then to ambient temperature in a desiccator.

B6 Apparatus

B6.1 Solvent removal device (see fig. 1)

B6.2 Teflon B24 bottle top, converts standard glass Winchester screw thread into a B24 socket for use with solvent removal device. (Available from Jencons Scientific Limited.)

B6.3.1 Glass Columns — Glass chromatography column approximately 100 mm × 10 mm I.D. (Quickfit CR 12/10 suitable)

B6.3.2 Preparation Fill a glass column to within 2 cm of the top with carbon tetrachloride. Add prepared Florisil with gentle tapping until it is packed to a depth of about 3 cm. Then add magnesium sulphate until the column is packed for approximately a further 1 cm.

B6.4 Bottle Rolling Machine Any rolling device capable of producing about 60 revs/min bottle speed.

B6.5 Rotary Evaporator

B6.6 Air Line — air cleaned by passage through molecular sieve and silica gel, line terminating in a fine jet of glass or metal and controllable such that the air jet indents the surface of the solvent without splashing (typically 200 ml/min from a jet of internal diameter 0.5 mm at a distance of 2 cm from the liquid).

B6.7 Standard laboratory glassware

B7 Sample Collection and Preservation

Representative sampling of oil-water mixtures is well known to be difficult and reference should be made to a general text on sampling (see other publications in this series (3)). However, it is reasonable to comment that the ideal situation would be piped waters or pumped sampling loops tapped directly into the sampling bottle and modifications of this should be evaluated critically.

If analysis is not carried out within 24 hours the sample should be acidified to pH2 or carbon tetrachloride added in the ratio 1:40. Wherever possible a note should be made of the weight or volume of preservative added (see note (a) Section B8).

B8 Analytical Procedure

Step	Procedure	Notes
B8.1	Extraction	
B8.1.1	Weigh the sample bottle plus sample liquid (W_1 g) (note a)	(a) It is usual to analyse 1 litre of sample and so its weight (W_1–W_2, see also B8.1.6) is obtained ± 1 g; this would be proportionately smaller for smaller volumes. Sometimes it is necessary to analyse a proportion of a much larger sample volume; under these circumstances the whole sample should be shaken vigorously and the 1 litre portion transferred to a bottle suitable to this procedure.
B8.1.2	To the sample liquid add approx. for each litre of liquid (i) 40 ± 1 g of sodium chloride (ii) 2 ± 0.1 ml of conc. H Cl Then add 25.0 ± 0.1 ml of carbon tetrachloride (see notes b and c)	(b) If acid has been added as a preservative further additions will not be required. Similarly if CCl_4 has been added further additions will be unnecessary. (c) If necessary use a pH meter and adjust to pH2 by the addition of conc HCl ensuring that no oil adheres to the electrode. 1,1,2 trichloro-, 1,2,2 trifluoro ethane may be used in most instances in place of carbon tetrachloride as an extractant (see also Section A12); the same conditions apply.
B8.1.3	Replace the bottle screw cap with the teflon B24 bottle cap and B24 glass stopper. Shake vigorously for one minute and roll for 30 minutes (note d)	(d) Any oil adhering to the bottle cap should be washed off with an aliquot of the carbon tetrachloride used for extraction.
B8.1.4	Decant most of the aqueous layer and run off the carbon tetrachloride into a small glass beaker by means of the solvent removal device (B6.1). The bottle should be rinsed with 2 × 10 (± 0.5) ml aliquots of carbon tetrachloride which are removed as above and added to the original extract in the beaker.	
B8.1.5	Dry the extract in the beaker by the addition of sufficient magnesium sulphate (note e)	(e) Alternatively plug a glass filter funnel with glass wool, add magnesium sulphate into the funnel and decant the extract through the funnel. Wash the magnesium sulphate thoroughly with a small quantity of carbon tetrachloride to finish.
B8.1.6	Weigh the empty sample bottle (W_2 g)	
B8.2	Clean-up procedure	
B8.2.1	Prepare a Florisil column as described in B6.3.2. Run off surplus carbon tetrachloride.	
B8.2.2	Run the extract through the column and rinse the beaker with 2 × 10 (± 0.5) ml of aliquots of carbon tetrachloride which are run through the column and add to the extract (note f)	(f) Care should be taken not to overload the column. The capacity is around 30 mg of fatty material. When all the extract is being cleaned it is suggested that a longer column is prepared.

Step	Procedure	Notes
B8.3	**Evaporation**	
	Evaporate the cleaned up extract from B8.2.2 to 2 ml ± 1 ml using a rotary evaporator.	
	Transfer the concentrated extract to a tared 25 ml beaker. Rinse the evaporator flask with 3 portions of 1.5 ml ± 0.2 ml of carbon tetrachloride and add the washings to the beaker.	
	Place the beaker on a steam bath and cautiously evaporate off the carbon tetrachloride using the air line. This step must be performed in an efficient fume cupboard.	
B8.3.1	Heat the beaker in an oven at 105°C ± 2°C for 15 minutes. Allow to cool in a desiccator and reweigh.	
B8.4	A blank determination should be performed with each batch of samples using distilled water and following the procedures in sections B8.1–B8.3. The weight (B g) should be noted.	
B8.5	**Calculation**	
	The concentraction of oil in the original aqueous sample may be calculated from the equation. (notes g and h)	(g) Allowance must be made for weight of added preservative.
	$C = \frac{W_4 - W_3 - B}{W_1 - W_2} \times 10^6$	(h) For most practical purposes mg/kg is equivalent to mg/l.
	Where C = conc. of oil in the aqueous sample in mg/kg	
	W_2 is the weight of the sample bottle in g.	
	W_1 is the weight of the sample bottle + sample in g.	
	W_3 is the weight of beaker in g.	
	W_4 is the weight of beaker + evaporated extract in g.	

C. Sources of Error

The attention which it is necessary to pay to sources of error depends on the accuracy required of the analytical results. Each method has sections dealing with interfering substances. In the case of Method A special attention is to be paid to temperature effects. Different temperatures give rise to different extraction efficiencies, adsorption efficiencies on Florisil and absorption coefficients. Particular care should be taken not to leave the cells containing the solvent solutions in the spectrophotometer because the solution will rise in temperature.

D. Checking the Validity of Analytical Results

Once the methods have been put into routine operation many factors may subsequently affect the validity of the analytical results. It is recommended that experimental tests of the validity should be made regularly. As a minimum, however, it is suggested that a prepared sample should be analysed in duplicate at the same time and in exactly the same way as normal samples. Such checks will be facilitated by plotting results obtained on quality control charts which will detect inadequate accuracy and will also allow the standard deviation of routine analytical results to be estimated.

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Printed in the UK for HMSO
Dd 718529 C12 1/84

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