The Determination of Oils and Fats in Waste Water by Filtration, Solvent Extraction and Gravimetry, 1987

(Tentative Method)

Methods for the Examination of Waters and Associated Materials

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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 These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print.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

1 July 1987

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 checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. 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 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. 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.

Determination of Oils and Fats in Waste Water by Filtration, Solvent Extraction and Gravimetry

Introduction

01 This method, like the majority of methods for the quantification of oils and fats is empirical. The materials determined are decided by the procedure used.

02 Because of the wide range of sources and properties of materials defined as natural oils and fats no one analytical method can be expected to determine all the substances so described. However as most show a high degree of solubility in light petroleum spirit (40–60°C) the method is based on extractability from water into that solvent under defined conditions.

03 Once extracted, the oil or fat may be subjected to further examination, such as by infra-red spectrophotometry and gas chromatography, and compared to standard materials, including those taken from the known or suspected source of the sample. If there is sufficient extract, this may be subjected to saponification (reference 10.1). The saponified extract may then be re-extracted with light petroleum spirit (40–60°C) after dilution with water. These techniques give an indication of the proportion of saponifiable material which is then more readily equatable to natural fats and oils.

04 The principal applications of the method will be for the analysis of industrial effluents and sewages.

05 The method forms part of a continuing series, which when complete can be used as part of a general co-ordinated scheme of analysis.

1. Performance Characteristics of the Method

1.1	Substance determined	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.
1.2	Type of samples	Effluents, sewages and other waste waters.
1.3	Basis of method	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.
1.4	Range of application	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 mg of eventual extract.

1.5 Recovery*

Mean Conc., mgl^{-1}		Standard Deviations of Recovery Converted to mgl^{-1}			
Added	Recovered	$1S_W$	$2S_B$	$3S_T$	Degrees of Freedom
50.43	46.04	4.5	NS	6.3	$8(S_T)$
505.4	463.9	14.5	NS	20.4	$8(S_T)$

NS = Not Significant

1.6	Limit of detection*	3.6 mg/l

1.7	Sources of error	See Section 3
1.8	Time required for analysis	3 hours per sample

* Obtained by Unilever PLC using deodorized palm oil.

$1S_W$—within batch
$2S_B$—between batch
$3S_T$—total

2. Principle

The sample of water is filtered through GFC paper. The material retained is then extracted in a soxhlet apparatus into light petroleum spirit (40–60°C). The solvent is then removed and the residue weighed.

3. Sources of Error

Other substances separable from water by filtration and soluble in light petroleum spirit (40–60°C), such as hydrocarbons and hydrocarbon oils, will be included in the extract. Therefore in strict terms the method does not measure the parameter of "natural fats and oils". However the method will be used most frequently for the analysis of industrial effluents in which the nature of the material being measured is more likely to be known. In other instances, further analysis may reveal the general characteristics of the extract. Within the method itself there are no major sources of error.

4. Hazards

Light petroleum spirit (40–60°C) and acetone are narcotic and highly flammable. Avoid inhalation, contact with skin and eyes, and ingestion. 2M hydrochloric acid is corrosive and should be handled with care. Contact with skin etc should be avoided.

5. Reagents

Analytical grade chemicals should be used, wherever possible.

5.1 Light petroleum spirit (boiling range 40–60°C). This should be re-distilled if analytical grade reagent is not available.

5.2 2M hydrochloric acid

5.3 Anhydrous magnesium sulphate.

5.4 Oxygen-free nitrogen.

5.5 Acetone.

6. Apparatus

6.1 Soxhlet apparatus and thimble (250 ml flask and water-cooled condenser as given in the diagram).

6.2 Buchner filtration apparatus.

6.3 Water Bath (boiling).

6.4 GFC filter papers—9 cm.

6.5 Heating mantle.

6.6 Tweezers.

6.7 Glass wool pre-washed with light petroleum spirit (40–60°C).

6.8 Filter Aid—Celite—Hyflo-super-cel ex BDH, or similar.

6.9 Muslin Cloth discs, 11 cm diameter.

7. Sample Collection and Preservation

Representative sampling of oil and water mixtures is difficult and reference should be made to a general text on sampling (reference 10.2). Natural oils and fats may degrade on storage, but no quantitive information is available; samples should be

analysed as quick as possible. If samples cannot be analysed immediately they should be acidified to pH 2 and stored between 2-5°C. Maximum recommended holding time is 24 hours.

8. Analytical Procedure

Step	Procedure	Notes
8.1	**Filtration**	
	Filter 500–1000 ± 5 ml of sample through a GFC filter paper in a thoroughly cleansed Buchner apparatus under vacuum. Note the volume of sample V ml.	
	The sample should be shaken thoroughly to ensure that the fat and oil are as homogeneous as possible and not adhering to the bottle surface. Keep the sample swirling whilst it is being measured out (note a).	(a) If the sample contains emulsified fats it may be acidified with 2M hydrochloric acid to a pH value of about 2. However acidification will break soaps into fatty acids and these will then be recovered by this method.
	If the sample is highly contaminated, problems may occur in the filtration. In these circumstances use one or more of the following modifications.	
	(i) a smaller sample volume. (ii) a filter aid maybe used to speed up filtration (see 6.8 and step 8.2). (iii) a larger size GFC filter paper (eg. 15 cm) may be used with the corresponding buchner filtration apparatus.	
8.2	If, due to filter blockage, it is necessary to use filter aid, this should be prepared as follows.	
	Disperse approximately 10 g filter aid in 1 litre of distilled water. Prepare a filter consisting of a muslin cloth disc overlaid with filter paper. Wet the paper and muslin, and press down the edges of the paper. Using a vacuum, pass 100 ml of filter aid suspension through the prepared filter and wash with 1 litre of distilled water. Apply vacuum until no more water passes through the filter. Proceed with the extraction as described in step 8.1.	
8.3	Using clean tweezers, transfer the filter paper to a soxhlet extraction thimble containing 1–2 g anhydrous magnesium sulphate.	
8.4	Wipe the buchner funnel with pieces of filter paper soaked in light petroleum spirit (40–60°C) in order to remove any remaining film of grease or solid material. Add these pieces of paper to the thimble.	
8.5	Place the thimble in the soxhlet apparatus.	
8.6	In order to remove any residual oil or fat adhering to the surface of the cylinder used for measuring out the sample, wash it with 20–30 ml of light petroleum (40–60°C).	
8.7	Add these solvent washings to the soxhlet thimble and then fill it with grease free glasswool.	

Step	Procedure	Notes
	Extraction	
8.8	Weigh a 250 ml flask to within ±0.1 mg (A grams). The flask should first be cleaned and dried as follows:— (i) wash thoroughly with hot detergent solution. (ii) rinse with clean water to remove detergent. (iii) rinse with acetone. (iv) Evaporate the acetone with a stream of nitrogen. (v) store in a desiccator.	
8.9	Add 200 ± 1 ml of light petroleum spirit (40–60°C) to the flask and connect to the soxhlet apparatus.	
8.10	Place the apparatus on a boiling bath and reflux for 2 hours at the rate of 20 cycles per hour. (note b).	(b) A heating mantle may be used.
	Drying	
8.11	Remove the soxhlet apparatus and evaporate off the light petroleum spirit (40–60°C) remaining in the 250 ml flask on the boiling water bath (note c).	(c) The volume requiring evaporation may be minimised by stopping the reflux just before the soxhlet empties as part of a cycle.
8.12	When the light petroleum has evaporated add 10 ± 0.5 ml acetone to the residue and evaporate again. Repeat this operation twice. (note d).	(d) This ensures that the residue does not contain moisture.
8.13	Pass a gentle stream of oxygen free nitrogen into the flask until all traces of acetone are removed.	
8.14	Remove the flask from the water bath or heating mantle, wipe the outside dry and place in a desiccator for one hour.	
8.15	Weigh the flask and residue to within ±0.1 mg (B grams).	
	Blank	
8.16	Solvent blanks should be carried out daily and when a new batch is started by repeating steps 8.8–8.15 but adding extra solvent of the same volume as used in 8.5. Obtain the blank weight of flask and residue (C grams). The blank value, determined as described above, should be less than 1 mg/l.	
	Calculation	
8.17	Total Fatty Matter (TFM) $mgl^{-1} = \frac{(B-A)-(C-A)\times 10^{-6}}{V}$	

9. Checking the Validity of Analytical Data

Once the method has been put into normal 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. Many types of test are possible and they should be used as appropriate. As a minimum, however, it is suggested that at least one sample of the waste water under consideration, of suitable concentration in each batch of analysis, be analysed in duplicate. The results obtained should then be plotted on a quality control chart which facilitates detection of inadequate precision and allows the standard deviation of routine analytical results to be estimated.

10. References

10.1 Department of the Environment Standing Committee of Analysts. Methods for Examination of Waters and Associated Materials. Classical Methods for the Characterisation of Oils, Fats and Waxes by Saponification, Hydroxyl, Iodine and Acid Values 1983. HMSO London 1984.

10.2 Department of the Environment Standing Committee of Analysts. Methods for Examination of Waters and Associated Materials. The Sampling of Oils, Fats, Waxes and Tars in Aqueous and Solid Systems 1983. HMSO London 1984.

11. Addresses for Correspondence

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

11.2 At the present, though based on work in several laboratories, thorough test data is not available; hence the tentative status of the method. Additional test data would be welcomed. Results should be sent to the same address.

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The Department of the Environment
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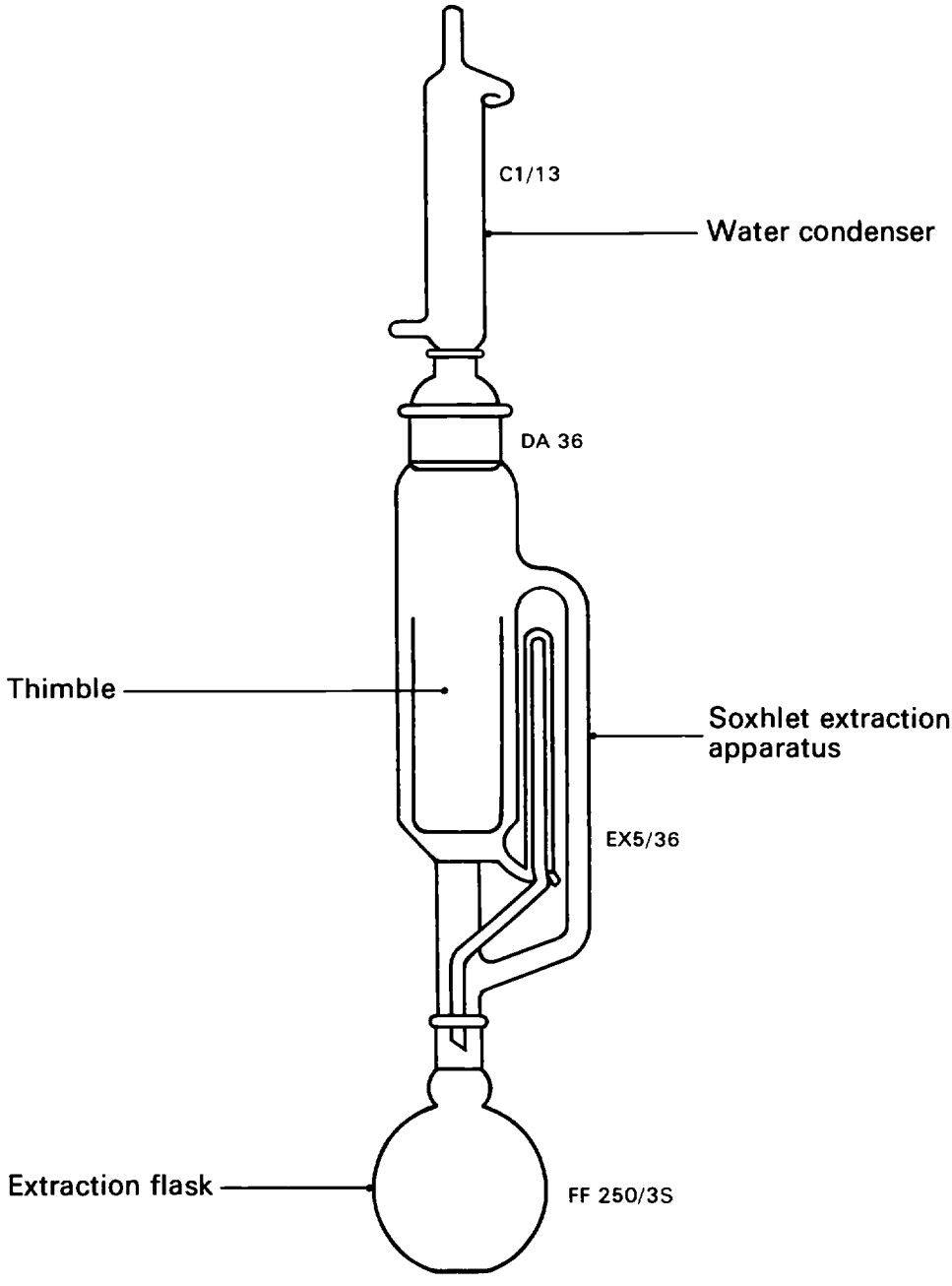
ENGLAND

Soxhlet apparatus



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3. Member of the Oils, Fats, Waxes and Tars Panel
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