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DRAFT ZANZIBAR NATIONAL STANDARD

Methods of Sampling and Test (Physical and Chemical) for Water and Wastewater - Part 1: Oil and Grease

ZANZIBAR BUREAU OF STANDARDS

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First Edition

Foreword

This draft Zanzibar National standard is presented to Water Quality Standards Technical Committee (TCE1) in order to be analysed and commented.

The Zanzibar Bureau of Standard (ZBS) was established under Standard Act No. 1 of 2011.

In the preparation of this standard, the reference was made to the following sources:

IS 3025 (Part 39):2021, *Methods of Sampling and Test (Physical and Chemical) for Water and Wastewater Part 39 Oil and Grease*

DRAFT FOR STAKEHOLDERS COMMENT

Introduction

Oil and grease are primarily composed of fatty matter of animal or vegetable origin and petroleum hydrocarbons. Hence, in the determination of oil and grease instead of quantifying a particular substance, a group of compounds with similar properties are determined quantitatively on the basis of their common solubility in hexane. The methods covered in this standard are suitable for assessment of biological liquids, mineral hydrocarbons, industrial wastewater or treated effluents containing these materials. The methods shall not be applicable to low boiling fractions that volatilize at temperatures below 85 °C.

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with ZNS 94, Rounding off numerical values.

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Methods of Sampling and Test (Physical and Chemical) for Water and Wastewater - Part 1: Oil and Grease

1 Scope

This Zanzibar National Standard prescribes the following methods for determination of oil and grease in water and wastewater:

- a) liquid-liquid partition-gravimetric method;
- b) partition infra-red method;
- c) soxhlet extraction method;
- d) extraction method for sludge samples;
- e) modified method for hydrocarbons; and
- f) solid-phase partition-gravimetric method.

Partition gravimetric method is applicable to the estimation of oil and grease in the range of 4-100 mg/L, partition infra-red method is applicable in the range of 1-50 mg/L, and soxhlet extraction method is applicable in the range of 20-200 mg/l in water and waste water.

Partition infra-red method is applicable for samples that might contain volatile hydrocarbons that otherwise would be lost in the solvent removal operations in the gravimetric method.

This standard also prescribes the method for estimation of petroleum hydrocarbon content in the extracted oil and grease.

2 Normative references

The following referenced documents are indispensable for the application of this Zanzibar National Standard. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5667-9, Water quality — Sampling — Part 9: Guidance on sampling from marine waters

ZNS 308, Water quality — Vocabulary

ZNS 356 (Part I), Water, sewage and Industrial effluents-Glossary of terms-Part 1

3 Terms and definitions

For the purposes of this document, the (terms and) definitions given in ZNS 308 and ZNS 356 (Part I) and the following shall apply.

3.1 oil and grease

any material recovered as a substance soluble in non-polar organic solvents like hexane.

4 Sampling and storage

Sampling and storage shall be done as prescribed in ISO 5667-9. Collect about 1 litre of a representative sample in a wide mouth glass bottle that has been rinsed with the solvent. Mark the sample level in the bottle. Acidify to pH 2 by adding either 1 : 1 HCl or 1 : 1 H₂SO₄. Collect separate samples for oil and grease determination. Loss of grease will occur on sampling equipment hence collection of a composite sample is not practical. Individual samples collected at prescribed time intervals should be analyzed separately to obtain average concentration over an extended period.

5 Liquid-liquid partition gravimetric method

5.1 Principle

Dissolved or emulsified oil and grease is extracted from water by intimate contact with hexane and estimation is made gravimetrically. Organic solvents sometimes form emulsions that are difficult to break. This method provides ways of handling such emulsions. Recovery of solvents is also mentioned.

5.2 Interferences

The solvent (hexane) can extract not only oil and grease but other organic substances that are soluble in it.

5.3 Apparatus

5.3.1 Separating Funnel — 1 litre capacity with teflon or equivalent stopcock.

5.3.2 Distillation Flask — Flat bottom of 250-mL capacity.

5.3.3 Water Bath — Capable of maintaining 85 °C.

5.3.4 Filter Paper — Whatman No. 40 or equivalent, 11 cm diameter.

5.3.5 Centrifuge — Capable of spinning at least four 100 mL glass centrifuge tubes at 2 400 rpm or more.

5.3.6 Centrifuge Tubes — 100 mL, glass.

5.3.7 Desiccator

5.3.8 Glass Funnel

5.3.9 Vacuum Pump

5.3.10 Distilling Adapter — With drip tip. Set up distillate recovery apparatus as shown in Fig. 1. Alternatively, a commercially available solvent recovery equipment may be used.

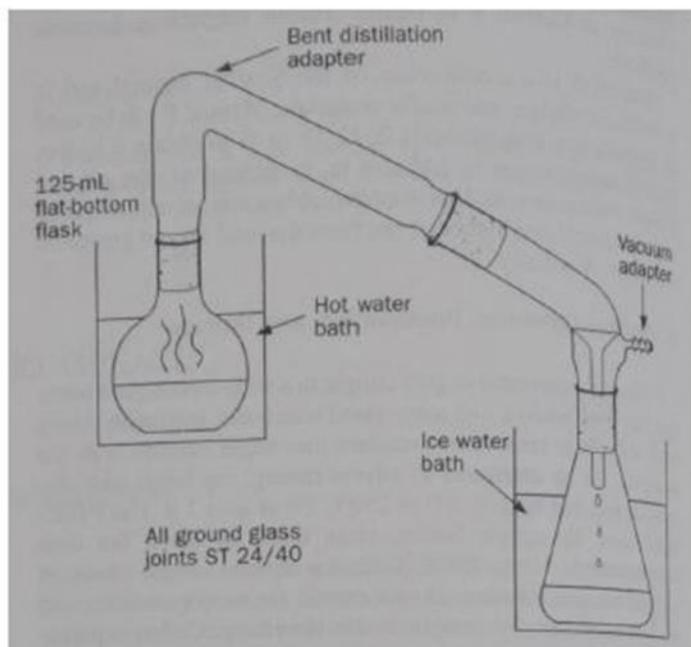


Figure 1: Distillate Recovery Apparatus

5.3.11 Ice Bath**5.3.12 Waste Receptacle** — For used solvent.**5.4 Reagents**

5.4.1 Hydrochloric Acid — 1 : 1. Mix equal volumes of acid and reagent water.

5.4.2 n-Hexane — 85 percent minimum purity, 99 percent minimum saturated C₆ isomers, residue less than 1 mg/L. Distill if necessary. Do not use any plastic tubing to transfer solvent between containers.

5.4.3 Sodium Sulphate — Anhydrous crystal (dried at 200-250 °C for 24 h).

5.4.4 Acetone — Residue less than 1 mg/L.

5.4.5 Hexadecane — 98 percent minimum purity.

5.4.6 Stearic Acid — 98 percent minimum purity.

5.5 Procedure

Transfer the acidified sample to a separating funnel. Carefully rinse the sample bottle with 30 mL of hexane and add the solvent washings to the separating funnel.

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Shake vigorously for about 2 min. However, if it is suspected that a stable emulsion will form, shake gently for 5 to 10 min. Let the layers separate. Drain aqueous layer and a small amount of organic layer into the original sample container. Drain the solvent layer through a funnel containing filter paper and 10 g Na₂SO₄, both of which have been rinsed with the solvent, into a clean, tared distillation flask.

If a clear solvent layer cannot be obtained and an emulsion of more than 5 mL exists, drain emulsion and solvent layers into a glass centrifuge tube and centrifuge for 5 min at approximately 2 400 rpm. Transfer the centrifuged material to separating funnel and drain solvent layer through a funnel containing filter paper and 10 g Na₂SO₄, both of which have been rinsed with the solvent, into a clean, tared distillation flask.

Put the separated aqueous layer into the separating funnel again. Extract two more times with 30 mL of solvent each time, but first rinse the sample container with the solvent. Collect the extracts in tared distillation flask and wash filter paper with an additional 10 to 20 mL of the solvent. Distil solvent from distillation flask over a water bath at 85 °C. To maximize solvent recovery, fit distillation flask with distillation adapter equipped with a drip tip and collect solvent in an ice-bath cooled receiver. When visibly all the solvent has been distilled off, remove distillation adapter and draw air through the distillation flask with applied vacuum for one minute. Remove the flask from water bath and wipe it dry from outside. Cool in a desiccator until the flask obtains a constant weight.

5.6 Calculation

$$\text{Oil and grease, mg/L} = \frac{M}{V} \times 100$$

where,

M = mass, in mg, of the residue
V = initial sample volume, in L.

5.6 Precision and Bias

Average recovery of 93 percent and precision (as relative standard deviation) of 8.7 percent.

6 Infrared spectroscopic method

6.1 Principle

The sample of water and wastewater is extracted with tetrachloroethylene (TCE) as extraction solvent followed by analysis by infra-red (IR) spectrometry using peak heights at $2930 \pm 5 \text{ cm}^{-1}$.

6.2 Apparatus

6.2.1 Separating Funnel — 2 litre capacity with Teflon or equivalent stopcock.

6.2.2 Infra-Red Spectrophotometer

6.2.3 Cells — Infra-red, silica/quartz (1 or 5 cm path length; for lower range, 5 cm path length will be appropriate).

6.2.4 Filter Paper — Whatman No. 40 or equivalent, 11 cm diameter.

6.2.5 Volumetric Flask — 100 mL.

6.2.6 Glass Funnel

6.2.7 Centrifuge — Capable of spinning at least four 100 mL glass centrifuge tubes at 2 400 rpm or more.

6.2.8 Centrifuge Tube — 100 mL glass (optional).

NOTE 1: Silicon grease should not be used for sealing purpose.

6.3 Reagents

Unless specified, all reagents should be of analytical grade and of high purity.

6.3.1 Hydrochloric Acid — See IS 265.

6.3.2 Tetrachloroethylene — Spectroscopic grade (minimum 99.5 percent purity).

6.3.3 Anhydrous Sodium Sulphate — Dried at 200 to 250 °C.

6.3.4 Reference Oil — Prepare a mixture by volume of 37.5 percent iso-octane, 37.5 percent hexadecane and 25 percent benzene. Store in a stoppered (preferably teflon or equivalent stopcock) 100 ml volumetric flask to prevent loss by evaporation.

6.4 Preparation of Calibration Standard

Add 1 mL of reference oil standard (see 6.2.4) in a 100 mL volumetric flask, stopper it and weigh it. Make up the volume to the mark with the solvent (6.2.2) and calculate the exact concentration, in mg/L.

6.5 Procedure

Transfer about 1 litre of the acidified sample (see 4) to a separating funnel and rinse the glass bottle with 20 mL of solvent and add the solvent washing to the separating funnel. Shake vigorously for about 2 min. However, if it is suspected that a stable emulsion will form, shake gently for 5 to 10 min. Let the layers separate. Drain aqueous layer and a small amount of organic layer into the original sample container. Drain the solvent layer through a funnel containing filter paper and 10 g Na₂SO₄, both of which have been rinsed with the solvent, into a clean, tared distillation flask. If a clear solvent layer cannot be obtained and an emulsion of more than 5 mL exists, drain emulsion and solvent layers into a glass centrifuge tube and centrifuge for 5 min at approximately 2 400 rpm. Transfer the centrifuged material to separating funnel and drain solvent layer through a funnel containing filter

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paper and 10 g Na₂SO₄, both of which have been rinsed with the solvent, into a clean, tared distillation flask.

Put the separated aqueous layer into the separating funnel again. Rinse the sample container with the solvent and then extract four times with 20 mL of solvent each time. Collect the combined extract in a 100 mL volumetric flask and adjust the final volume to 100 mL with solvent. Prepare a method blank with reagent grade water adopting same extraction process (without reference oil). Scan the standards and samples from 3 200 to 2 700 cm⁻¹. Measure absorbance of standards at peak height at 2930 ± 5 cm⁻¹ on solvent tetrachloroethylene background. Similarly, measure the absorbance of samples at same peak height with the method blank background. Prepare a calibration curve of absorbance (abscissa) versus concentration of standards (ordinate). If the absorbance of a sample exceeds that of the highest standard concentration, dilute the sample as required.

NOTE 1: The recovery of spiking standard at minimum detected level should be 100 ± 30 percent

6.6 Calculation

$$\text{Oil and grease, mg/L} = \frac{A \times 1000}{V}$$

where

A = mass of oil grease in the extract as determined from calibration curve, in mg

V = volume of the sample, in ml.

7 Soxhlet extraction method

7.1 Principle

The sample is subjected to extraction in a soxhlet apparatus with hexane. The residue left after the evaporation of solvent is weighed. Compounds volatilized at or below 103 °C will be lost when filter is dried. The method is empirical and reproducible results can be obtained only by adherence to all the details.

7.2 Apparatus

7.2.1 Soxhlet Apparatus

7.2.2 Vacuum Pump

7.2.3 Buchner Funnel — 12 cm diameter.

7.2.4 Electric Heating Device

7.2.5 Paper Extraction Thimble

7.2.6 Filter Paper — Whatman No. 40 or equivalent, 11 cm diameter.

7.2.7 Muslin Cloth Discs — 11 cm diameter.

7.2.8 Glass Beads or Glass Wool

7.2.9 Distilling Adapter with Drip Tip.

7.2.10 Ice Bath

7.2.11 Waste Receptacle — For used solvent.

7.2.12 Desiccator

7.2.13 Water Bath — Capable of maintaining 85 °C.

7.3 Reagents

7.3.1 Diluted Hydrochloric Acid — 1 : 1 (V/V).

7.3.2 n-Hexane — See 6.2.2.

7.3.3 Diatomaceous Silica Filter Aid Suspension — 10 g/L, distilled water.

7.4 Procedure

Prepare a filter consisting of a muslin cloth disc overlaid with filter paper. Wet the cloth and paper. Pass 100 ml of filter aid suspension (see 7.3.3) through the prepared filter under vacuum and wash with 1 litre of distilled water. Filter the acidified sample (pH ≤ 2). Apply vacuum until no more liquid sample passes through filter paper. Using forceps, transfer the filter paper to a watch glass. Add material adhering to edges of muslin cloth disc. Wipe sides and bottom of collecting vessel and Buchner funnel with filter paper soaked in solvent, taking care to remove all films caused by grease and collect all the solid material. Add pieces of filter paper to filter paper on watch glass. Roll all filter papers containing sample and put into a paper extraction thimble. Add any pieces of material remaining on watch glass. Wipe the watch glass with a filter paper soaked in solvent and place it in the thimble. Dry the filled thimble at 103 °C for 30 min in an oven. Fill the thimble with glass wool or small glass beads. Weigh the extraction flask and add 100 mL solvent. Extract oil and grease in a Soxhlet apparatus, using hexane at a rate of 20 cycles per hour for four hours counting from first cycle. Distil solvent from extraction flask over a water bath maintained at 85 °C. Place the flask on a water bath at 85 °C for 15 min and use distilling adapter and ice bath for solvent recovery. Draw air through the extraction flask by vacuum for the final 1 minute. Cool the flask in a desiccator for 30 min (till it reaches constant weight) and weigh.

7.5 Calculation

$$\text{Oil and grease, mg/L} = \frac{M \times 1000}{V}$$

Where

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M = mass, in mg, of the residue
V = volume, in ml, of the sample

8 Extraction method for sludge samples

8.1 Principle

Drying acidified sludge by heating leads to low results. The sludge is dried by using magnesium sulphate monohydrate. After drying the sludge is extracted with n-hexane.

8.2 Apparatus

8.2.1 Soxhlet Apparatus

8.2.2 Vacuum pump

8.2.3 Buchner Funnel — 12 cm diameter.

8.2.4 Electric Heating Device

8.2.5 Paper Extraction Thimble

8.2.6 Filter Paper — Whatman No. 40 or equivalent, 11 cm diameter.

8.2.7 Muslin Cloth Discs — 11 cm diameter.

8.2.8 Water Bath — Capable of maintaining 85 °C.

8.2.9 Glass Beaker — 150 mL.

8.2.10 Glass Beads or Glass Wool

8.2.11 Distilling Adapter with Drip Tip

8.2.12 Ice Bath

8.2.13 Waste Receptacle — For used solvent.

8.2.14 Desiccator

8.2.15 Porcelain Mortar and Pestle

8.3 Reagents

8.3.1 Hydrochloric Acid Concentrated

8.3.2 n-Hexane — See 6.2.2.

8.3.3 Magnesium Sulphate Monohydrate — Prepare $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ by drying a thin layer overnight in an oven at 150 °C.

8.4 Procedure

If the sample has not been acidified previously add 1 ml concentrated HCl/80 g of sample. Weigh 20 ± 0.5 g of wet sludge (for which dry-solids content is known) sample in a 150 mL beaker. Acidify to pH 2 or lower using conc. HCl, generally 0.3 mL is sufficient. Add 25 g of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ and stir to a smooth paste and spread on sides of beaker for subsequent easy removal. After 15–30 min, it solidifies, then remove and grind to a fine powder in a porcelain mortar. Add powder to a paper extraction thimble. Wipe beaker and mortar with small piece of filter paper soaked in solvent and place it in thimble. Repeat once more. Fill the thimble with glass wool or small glass beads. Weigh the extraction flask and add 100 mL solvent. Extract oil and grease in a Soxhlet apparatus, using hexane at a rate of 20 cycles per hour for four hours counting from first cycle. Distil solvent from extraction flask over a water bath maintained at 85 °C. Place the flask on a water bath at 85 °C for 15 min and use distilling adapter and ice bath for solvent recovery. Draw air through the extraction flask by vacuum for the final 1 min. Cool the flask in a desiccator for 30 minutes (till it reaches constant weight) and weigh.

8.5 Calculation

Oil and grease as % of dry solids = $(M \times 100) \div (\text{weight of wet sludge in g} \times \text{dry solids fraction})$

where

M = mass, in g, of the residue.

8.6 Precision analysis of six replicate samples of sludge yielded a standard deviation of 4.6 percent.

9 Modified method for hydrocarbons

9.1 Principle

To estimate the petroleum hydrocarbon content of oil and grease this modified method is used. Silica gel has the ability to adsorb all constituents of oil and grease except hydrocarbons. The material not adsorbed by silica gel is designated as hydrocarbons by this method.

9.2 Interference

The method is not accurate for the reason that any compound other than hydrocarbon and fatty matter recovered by the solvent interfere by coming either in hydrocarbon part or in fatty matter.

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9.3 Apparatus

9.3.1 Magnetic Stirrer with TFE Coated Stirring Bars

9.3.2 Glass Funnel

9.3.3 Filter Paper — Whatman No. 40 or equivalent, 11 cm diameter.

9.3.4 Desiccator

9.4 Reagent

9.4.1 n-Hexane — See 6.2.2.

9.4.2 Silica Gel — 75 to 150 micron size, dried at 110 °C for 24 hours and stored in tightly sealed container is required.

9.5 Procedure

Use the oil and grease extracted by any of the above methods. When only hydrocarbons are of interest introduce this procedure in any of the above methods before the final measurement. When hydrocarbons are to be measured after determining total oil and grease, redissolve the extracted oil and grease in 100 ml n-Hexane. To the extracted solution, add 3 g of silica gel/100 mg total oil and grease. Stopper the container and stir gently for 5 min. Filter the solution through filter paper and wash silica gel and filter paper with 10 ml of solvent. Collect the filtrate. Distil off the solvent from the filtrate as described in 5.5 and weigh the residue as hydrocarbons.

9.6 Calculation

$$\text{Hydrocarbons, mg/L} = \frac{M \times 1000}{V}$$

where

M = mass, in mg, of residue; and

V = volume, in ml, of sample.

9.7 Precision and Bias

For 10 synthetic organic extracts containing a wide variety of petroleum products, average recovery was 97.2 percent. Reagent water containing 20 mg/L each of hexadecane and stearic acid, single laboratory and interlaboratory method validation study resulted in average recovery of 87 percent and precision (as relative standard deviation) of 13 percent.

10 Solid phase partition gravimetric method

10.1 Principle

Dissolved or emulsified oil and grease is extracted from water by passing through a solid-phase extraction (SPE) disc and then eluted using n-Hexane. The method is not applicable to materials that volatilize below 85 °C or crude and heavy fuel oils containing a significant percentage of material not soluble in n-Hexane. The method may be especially useful for samples that tend to form difficult emulsions during extraction process.

10.2 Apparatus

10.2.1 SPE Apparatus, 90 mm.

10.2.2 Oil and Grease SPE Disc, 90 mm.

10.2.3 Distillation Flask Flat Bottom — 250 ml capacity.

10.2.4 Water Bath — capable of maintaining 85 °C.

10.2.5 Distilling Adapter with Drip Tip

10.2.6 Ice Bath

10.2.7 Waste Receptacle — For used solvent.

10.2.8 Filter Paper — Whatman No. 40 or equivalent, 11 cm diameter.

10.2.9 Desiccator

10.2.10 Glass Funnel

10.2.11 Apparatus for Distillation, and

10.2.12 Vacuum Pump

10.3 Reagents

10.3.1 n-Hexane — See 6.2.2.

10.3.2 1 : 1 HCl (V/V)

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10.3.3 Anhydrous Sodium Sulphate

10.3.4 Methanol AR

10.3.5 Acetone — Residue less than 1 mg/L.

10.3.6 Standard Solution — Hexadecane/stearic acid 1 : 1 w/w in acetone at 2 mg/mL each. Take 200 ± 2 mg stearic acid and hexadecane each in a 100 mL volumetric flask and fill up to mark with acetone (the solution may require warming for complete dissolution of stearic acid).

After the hexadecane and stearic acid have dissolved, transfer solution to a 100 to 150 ml vial with TFE lined stopper. Mark solution level on the vial and store in dark at room temperature. Immediately before use, make up the volume to the mark with acetone, if required, and warm to re-dissolve any visible precipitate.

10.4 Procedure

Acidify the water/wastewater sample to pH 2 or lower with 1 : 1 HCl or 1 : 1 H₂SO₄. Assemble the SPE apparatus and disc and condition disc as per manufacturer's instructions. Extract sample at an optimum flow rate of 100 ml/min, faster extraction rate will reduce recovery. Dry the disc completely before elution. Acetone rinse may be used for drying but will result in lower recoveries. Carefully control vacuum during elution with n-hexane to allow the solvent to penetrate the disc completely (vacuum of 20.3 cm Hg). Apply vacuum to draw a slow stream of n-hexane through the disc. Let disc dry before repeating elution with a second portion of n-hexane. Pour combined eluent through a glass funnel containing a filter paper and sodium sulphate both of which have been rinsed with solvent, into a clean tared distillation flask. Rinse collection vial and Na₂SO₄ funnel with n-hexane and add the rinse to the distillation flask. Distil solvent and measure as per procedure described in 5.5.

10.5 Calculations

$$\text{Oil and grease, mg/L} = \frac{M \times 1000}{V}$$

where

M = mass, in mg, of the residue; and

V = volume, in ml, of the sample taken.

10.6 Precision and Bias

In a comparison of laboratory-fortified sample (n = 46) with additions of approximately 20 mg/L each hexadecane and stearic acid and analysed by both automated and manual SPE systems, recoveries of 87.1 percent \pm 7.8 percent and 92.5 percent \pm 4.4 percent on 10 percent fortified reagent water samples.

Precision for wastewater may vary depending on the matrix.

Bibliography

Standard Methods for the Examination of Water and Wastewater published by the American Public Health Association, Washington, USA, 22nd Edition, 2012.

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