

Method for

Determination of water in insulating oils, and in oil-impregnated paper and pressboard

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- Association of Consulting Engineers
- Beama Transmission and Distribution Association
- British Railways Board
- Electricity Supply Industry in England and Wales
- ERA Technology Ltd.
- Institute of Petroleum
- Institution of Electrical Engineers
- London Transport Executive

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- British Lubricants Federation Limited
- Electric Cable Makers' Confederation
- Electric Cable Makers' Confederation (Supertension Cables Group)

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National foreword

This British Standard has been prepared under the direction of the General Electrotechnical Engineering Standards Committee. It is identical with IEC 733:1982 “*Determination of water in insulating oils, and in oil-impregnated paper and pressboard*” published by the International Electrotechnical Commission (IEC).

Terminology and conventions. The text of the International Standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards; attention is drawn especially to the following.

The comma has been used as a decimal marker in Figure 3, Figure 6 and Figure 7. In British Standards it is current practice to use a full point on the baseline as the decimal marker.

Cross-references

International Standard	Corresponding British Standard
IEC 567:1977	BS 5574:1978 <i>Guide for the sampling of gases and of oil from oil-filled electrical equipment and for the analysis of free and dissolved gases</i> (Identical)

The Technical Committee has reviewed the provisions of IEC 296, IEC 475, ISO 383 and ISO 641, to which reference is made in the text, and has decided that they are acceptable for use in conjunction with this standard. Related British Standards are BS 148, BS 5263, BS 572 and BS 2761 respectively.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 16, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

1 Scope

This standard applies to the determination of water in insulating oils and in oil-impregnated paper and pressboard.

Section 1 of this standard describes the determination of water in new and used insulating oils over the concentration range 2 mg/kg to 100 mg/kg. The precision data given in Clause 12 apply only to new oils with viscosity less than 20 mm²/s at 40 °C.

NOTE 1 For used oils, the accuracy of the method may be affected by the presence of contaminants and degradation products.

NOTE 2 The experimental details of the method have been designed to be particularly suitable for mineral oils complying with IEC Publication 296: Specification for New Insulating Oils for Transformers and Switchgear. For use with other oils, modifications to the solvent proportions or sample size may be required.

Section 2 describes methods for the determination of water in oil-impregnated paper and pressboard over the range 0.1 % to 20 % by mass.

Appendix A provides guidelines to the sampling of oil-impregnated paper and pressboard.

Appendix B contains an alternative method based on the extraction of water by means of a nitrogen stream which may be useful to determine the water content in paper impregnated with very viscous oils.

Section 1. Determination of water in insulating oils

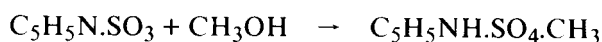
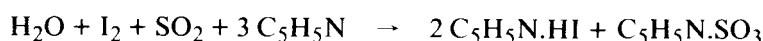
2 Outline of method

A chloroform-methanol mixture is introduced into the titration vessel and the water in this solvent mixture is reacted with Karl Fischer reagent. The sample is then added to the solvent and the mixture again titrated with Karl Fischer reagent. The Karl Fischer reagent is standardized against an accurately metered amount of water. The end-point of the titration is detected electrometrically using platinum electrodes immersed in the solution across which a specified potential difference is applied. The presence of water in the titration mixture causes polarization of the cathode, thus opposing the passage of current. At the end-point of the titration, excess Karl Fischer reagent depolarizes the cathode giving an increase in current which is shown on a microammeter in series with the electrodes.

3 Chemistry

The method is based on the reaction of water with a solution of iodine and sulphur dioxide in a pyridine-methanol mixture (Karl Fischer reagent).

Actual reactions are complex, but are essentially of water with iodine and sulphur dioxide and may be expressed as:



NOTE Pyridine can be replaced by other chemicals to control the pH during the reaction.

4 Reagents and auxiliary materials

4.1 Karl Fischer reagent, water equivalent 2.5 mg water/ml to 5 mg water/ml, approximately (see Note 1).

4.2 Methanol, analytical reagent grade, water content approximately 0.05 % (see Note 2).

4.3 Chloroform, analytical reagent grade, water content approximately 0.05 % (see Note 2).

4.4 Magnesium perchlorate, dried, used as desiccant.

4.5 Lubricating grease, polytetrafluoroethylene filled petroleum or fluorinated hydrocarbon types.

NOTE 1 Some batches of Karl Fischer reagent may not be suitable because they do not show the very rapid increase in the electrode current referred to in the note of Sub-clause 8.6.

NOTE 2 A small quantity of water has to be present in the solvent for the reaction to proceed satisfactorily. The reagent qualities specified have been found suitable, but should not be further dried.

NOTE 3 **WARNING!** Certain reagents may be detrimental to human health and must be handled with proper care.

5 Apparatus (see Figure 1, Figure 2, Figure 3 and Figure 4, pages 11 to 13)

5.1 Karl Fischer electrometric titration apparatus (Figure 1) consisting of:

- a) *piston burette*, graduated in increments of 0.005 ml or less, with a jet made from 0.5 mm bore capillary tubing. The construction of a suitable jet is shown in Figure 2. The capillary tubing below the conical ground joint 10/19 should be so bent, and of such a length, that the tip of the jet remains immersed in the liquid at all times and does not discharge into the vortex formed when the liquid is stirred.
- b) *flanged titration vessel*, nominal 250 ml capacity, inside diameter 50 mm. A drainage tap fitted to the base is an advantage when the vessel is to be emptied. The titration vessel should be shielded from direct sunlight when in use.
- c) *titration vessel lid*, flanged to match the titration vessel, with at least four sockets, one of which should be at least a conical ground joint 14/23 to facilitate the addition of solid samples. One socket should be fitted with a rubber septum.
- d) *electrodes*, pure platinum or platinum alloy wire, formed into almost closed loops and anchored by fusion into a glass tube carrying a conical ground joint 10/19 at the upper end, so that the lowest part of the loops is approximately 20 mm above the base of the titration vessel and positioned so that the loops are always completely immersed. The construction and dimensions of the electrodes are shown in Figure 3, page 12.

NOTE The electrode is particularly robust when 1 mm diameter wire is used and has been designed for use also with solid samples. If, however, only liquid samples are to be tested, the free end of the wire need not be anchored and smaller diameter wire may be used.

The distance between the electrode wires is unimportant but care should be taken, when using small diameter wire, to prevent accidental short-circuiting. If anchored loops are made, the maximum width of the loops should not exceed 5 mm to allow the electrode assembly to pass through a conical joint 10/19.

The electrode current at the inflexion point of the sensitivity curve is mainly determined by the surface area of the cathode and to a much smaller extent by the stirring speed. A suitable surface area is obtained by forming loops of inside diameter 2.2 mm for 1 mm diameter wire. The table in Figure 3 gives, for various diameters of wire, the lengths of exposed wire required to give the same surface area. Other values can be found by interpolation.

- e) *electromagnetic stirrer*, capable of maintaining a reasonably constant speed ($\pm 10\%$) within the range 300 rev/min to 1 000 rev/min throughout the determination, driving a glass or polytetrafluoroethylene coated stirring bar, made of iron, approximately 25 mm long.

NOTE The electromagnetic stirrer should be sufficiently powerful to prevent the stirring speed falling by more than 10 % when the oil sample is added to the solvent.

Any stirring speed within the range specified may be selected; once chosen, the stirring speed for all determinations should be maintained within $\pm 10\%$.

- f) *reservoir* for Karl Fischer reagent, black-painted or brown glass of suitable capacity.
- g) *electrometric circuit* as shown in Figure 4, page 13, (see also Appendix C).

NOTE Commercial instruments may use proprietary circuiting. These can be used provided their sensitivity and performance are not worse than indicated in this standard.

- h) *drying tubes* for titration vessel and reagent reservoir.

5.2 Glass syringes, graduated, of suitable capacities, fitted with stainless steel canulas, are used for sample transfer. The use of a syringe reduces the pick-up of atmospheric water vapour which causes errors if the sample is introduced by pouring directly from the sample container.

5.3 Chromatographic syringe, calibrated, 10 μ l capacity, needle length at least 150 mm, for calibration of Karl Fischer reagent.

6 Preparation of apparatus

6.1 Syringes should be dismantled and washed free of traces of previous samples, either with a suitable detergent solution, soapy water or a chlorinated hydrocarbon solvent, depending on the nature of the samples, rinsed thoroughly with warm water, then deionized water and finally, after draining, with methanol. Dry the clean syringes in a well-ventilated oven at $115 \pm 5^\circ\text{C}$ for at least 1 h, then cool to room temperature in a desiccator.

6.2 Karl Fischer apparatus: ensure that all joints in glassware and tubing are properly made and lightly coated with grease (see note of Figure 1). Check that the stirrer bar in the titration vessel will not contact the burette jet tip or electrodes when revolved. Fit the Karl Fischer solution reservoir to the burette and check that the desiccant in all drying tubes is in good condition, i.e. white and crystalline. (The desiccant will normally require changing at least every fourteen days).

7 Sampling methods for oils

7.1 Routine sampling

For routine tests the sampling methods described in Clause 2 and Sub-clause 3.1 of IEC Publication 475: Method of Sampling Liquid Dielectrics, shall be used.

7.2 Recommended sampling

For better accuracy, and particularly where the moisture content is very low, the procedure described in Sub-clause 3.2 and Appendix B of IEC Publication 567: Guide for the Sampling of Gases and Oil from Oil-filled Electrical Equipment and for the Analysis of Free and Dissolved Gases, shall be used.

8 Procedure

8.1 Fill the burette with Karl Fischer reagent, then empty it back into the reservoir. Swirl the content of the reservoir gently but thoroughly, taking care not to impose any strain on the glass tubing connections. Repeat this procedure three more times; the burette will now be dry and the reagent homogeneous. Refill the burette.

8.2 Turn tap 8 (see Figure 1, page 11) to connect the burette to the jet and flush the jet with the contents of the burette. Discard the reagent in the titration vessel and refill the burette to the zero graduation.

8.3 Add 75 ml of chloroform-methanol mixture (1 : 1 by volume) to the titration vessel.

8.4 Switch on the magnetic stirrer, and adjust to a speed within the range mentioned in Item e) of Sub-clause 5.1.

8.5 With the three-way switch in position A (Figure 4, page 13), adjust the "Millivolts control" to give a microammeter reading of 100 μA (equivalent to a circuit potential of 200 mV).

8.6 With the switch in position B, titrate the solvent mixture in the titration vessel with Karl Fischer reagent until the microammeter maintains a reasonably steady reading of about 50 μA . Switch to position C and continue titrating until the microammeter maintains a mean reading of $70 \pm 5 \mu\text{A}$ which does not drop more than 2 μA in 4 min. Note the meter reading, allowing for any oscillations that may occur. Fill the burette to the zero graduation.

NOTE During the initial stage of the titration of the residual water in the solvent, addition of Karl Fischer reagent causes a very rapid increase in the electrode current, followed by a fairly rapid fall. As the titration progresses, the current fluctuations becomes much less rapid and the rotary switch can be turned to position C.

With some electrodes, the current at the end-point may oscillate around a mean value by up to $\pm 2 \mu\text{A}$. The titration should be continued until this mean value is $70 \pm 5 \mu\text{A}$, (i.e. the mean value should be between 65 μA and 75 μA , disregarding the oscillations) and the downward drift of the mean value is less than 2 μA in 4 min.

8.7 With samples which have been collected in glass bottles, fill a syringe with oil, keeping the tip of the cannula well below the surface of the oil. Replace the top of the glass bottle immediately. Hold the syringe vertically, with the cannula uppermost, discharge all air bubbles and discard the contents of the syringe. Refill the syringe and weigh to the nearest 0.1 g. With samples which have been collected in a syringe, discharge approximately 2 ml to flush out the cannula and weigh, the syringe to the nearest 0.1 g.

8.8 Inject a quantity of oil into the titration vessel via the septum cap and re-weigh the syringe. Record the mass M , in grammes, of sample injected. The quantity of oil injected may be varied according to the approximate moisture content of the oil, if known. A range of 5 g to 25 g is suggested.

8.9 Titrate the moisture with Karl Fischer reagent until the microammeter needle remains at the reading noted in Sub-clause 8.6. Record the volume a in millilitres.

8.10 Carry out a duplicate determination by emptying the titration vessel and repeating the steps described in Sub-clauses 8.3 and 8.6 to 8.9.

8.11 Without emptying the vessel after the second determination, proceed immediately with the standardization of the Karl Fischer reagent as described in Clause 9.

9 Standardization of Karl Fischer reagent

9.1 Refill the burette to the zero position.

9.2 Fill a 10 μl chromatographic syringe with deionized water.

9.3 Inject the water into the titration vessel, taking care not to depress the plunger of the syringe while passing the needle through the septum cap. Submerge the needle tip below the surface of the liquid mixture before injection of the water. Record the quantity of water injected in milligrammes.