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ISO 10101-2

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Natural gas — Determination of water by the Karl Fischer method —

Part 2: Titration procedure

Gaz naturel — Dosage de l'eau par la méthode de Karl Fischer —
Partie 2: Méthode titrimétrique

Reference numbe
ISO 10101-2:1993(E

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 10101-2 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Sub-Committee SC 1, *Analysis of natural gas*.

ISO 10101 consists of the following parts, under the general title *Natural gas — Determination of water by the Karl Fischer method*:

— *Part 1: Introduction*

— *Part 2: Titration procedure*

— *Part 3: Coulometric procedure*

Annex A forms an integral part of this part of ISO 10101.

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Natural gas — Determination of water by the Karl Fischer method —

Part 2:
Titration procedure

WARNING — Local safety regulations must be taken into account, when the equipment is located in hazardous areas. Due to the toxicity and odour of pyridine, the user should ensure that there is adequate ventilation.

1 Scope

This part of ISO 10101 specifies a titrimetric procedure for the determination of water content in natural gas. Volumes are expressed in cubic metres at a temperature of 273,15 K (0 °C) and a pressure of 101,325 kPa (1 atm). It applies to water concentrations between 5 mg/m^3 and 5 000 mg/m^3.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 10101. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 10101 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 383:1976, *Laboratory glassware — Interchangeable conical ground joints.*

ISO 7504:1984, *Gas analysis — Vocabulary.*

ISO 10101-1:1993, *Natural gas — Determination of water by the Karl Fischer method — Part 1: Introduction.*

ISO 10101-3:1993, *Natural gas — Determination of water by the Karl Fischer method — Part 3: Coulometric procedure.*

3 Principle

A measured volume of gas is passed through a cell containing a relatively small volume of absorbent solution. Water in the gas is extracted by the absorbent solution and, subsequently titrated with Karl Fischer reagent. The design of the cell and the absorbent solution are chosen so as to ensure efficient collection of the water at the high flowrates necessary.

The principle and chemical reactions of the Karl Fischer method are given in ISO 10101-1:1993, clauses 3 and 4; interferences are also described in clause 4 of ISO 10101-1.

Clause 4 of ISO 10101-1:1993 describes interfering substances which may be present in natural gas and corrections for the interference of hydrogen sulfide and mercaptans.

4 Reagents

4.1 Kark Fischer reagent, of which the water equivalent is approximately 5 mg/ml.

NOTE 1 For most applications, commercially available Karl Fischer reagent with a water equivalent of approximately 5 mg/ml has been found adequate. The reagent may be provided as two solutions which are mixed before use.

If required, make up the reagent in the following way.

4.1.1 Components

4.1.1.1 Methanol, with a water content of less than 0,01 % (*m/m*). Use commercially available dry methanol or methanol dried in the laboratory by one of the following procedures.

a) Place 2 litres of methanol in a two-neck 3 litres flask and add 10 g of magnesium turnings. Add a crystal of iodine, connect the flask to a reflux condenser and leave overnight. Next day, add a further 5 g of magnesium turnings and reflux for 1 h. Connect the top of the reflux condenser to a still head, a double surface condenser and a collection flask. Disconnect the water flow through the condenser originally used for reflux, and distil the contents of the flask. Discard the first 150 ml of condensate. Distil the rest into dried 1 litre flasks. Vent the system through a drying tube during distillation.

b) Dry the methanol over a freshly activated molecular sieve[1].

4.1.1.2 2-Methoxyethanol, with a water content of less than 0,01 % (*m/m*).

NOTE 2 This can be used as an alternative to methanol (4.1.1.1), with a lower vapour pressure and therefore less losses due to evaporation during sampling of the gas.

4.1.1.3 Pyridine, anhydrous.

4.1.1.4 Sulfur dioxide, liquefied and dry.

4.1.1.5 Iodine.

4.1.2 Preparation

Measure 300 ml of dry methanol (4.1.1.1) or 2-methoxyethanol (4.1.1.2) and 110 ml of anhydrous pyridine (4.1.1.3) into a 750 ml conical flask. Slowly pass liquid sulfur dioxide (4.1.1.4) into this solution, mixing carefully until the increase in weight is 43 g. Cool this solution in a freezing mixture. When cool, add sufficient iodine (4.1.1.5) to give a permanent light brown colour. Then add 63 g of iodine and swirl until dissolved. Make up to 500 ml with dry methanol or 2-methoxyethanol. Leave standing in the stoppered conical flask for 24 h before use.

NOTES

3 If required, the reagent may be diluted with pyridine.

4 For the determination of very small amounts of water, is preferable to use freshly prepared reagent.

5 Commercial reagents, when aged, may give a slow response near the end point.

4.2 Absorbent solution, prepared in the following way.

4.2.1 Components

4.2.1.1 Ethylene glycol, with a water content less than 0,1 % (*m/m*).

4.2.1.2 Sulfur dioxide, liquefied and dry.

4.2.1.3 Pyridine, anhydrous.

4.2.1.4 Karl Fischer reagent, (see 4.1).

4.2.2 Preparation

Slowly add 20 g of sulfur dioxide (4.2.1.2) to 180 ml of anhydrous pyridine (4.2.1.3), while mixing carefully (solution A).

To prepare the absorbent solution, add 55 ml of dry ethylene glycol (4.2.1.1), 55 ml of Karl Fischer reagent (4.2.1.4) and 73 ml of solution A to a round bottomed flask. Boil under reflux for 10 min with a drying tube on the condenser, and then cool.

5 Apparatus

5.1 Karl Fischer apparatus, as described in annex A.

5.2 Wet-test gas meter, accurate to ± 1 % of the volume passed.

5.3 Guard tube, or **Durand bottle**, packed with anhydrous calcium chloride (or another suitable drying agent).

NOTE 6 This is used to prevent back diffusion of water vapour from the gas meter to the titration cell.

5.4 Titration cell, as shown in figure A.1.

5.5 Glass syringe, of 20 ml.

NOTE 7 Absorbent solution is most easily added to and removed from the cell by means of a 20 ml graduated syringe with a 6 % (Luer) fitting and hypodermic needles of suitable length and 1 mm to 2 mm bore.

5.6 Syringe, with a fixed needle, of 10 µl, for standardization of the Karl Fischer reagent.

1) Molecular sieves of type 4A (0,4 nm pore diameter) or type 5A (0,5 nm pore diameter) are an examples of a suitable products available commercially. This information is given for the convenience of users of this part of ISO 10101 and does not constitute an endorsement by ISO of these products.

6 Standardization of the Karl Fischer reagent

Standardize the Karl Fischer reagent daily or before use, as appropriate.

6.1 Using a dry syringe, introduce sufficient absorbent solution (4.2) to cover the electrodes in the apparatus (5.1). Switch on the apparatus and start the stirrer motor. Add the Karl Fischer reagent (4.1) until the needle settles down at a position near zero. When this point is reached, cease additions, since additions of large amounts of reagent will only move the electrometer about 0,02 V. To achieve maximum sensitivity at this first stable point, adjust the zero control until the electrometer needle is at zero. Shake the cell several times so that all the internal surfaces are wetted. Once again, adjust to the zero position by adding more reagent. Repeat the procedure until the needle remains steady at the zero position for at least 30 s.

NOTE 8 The meter needle will remain at zero for at least 30 s when the titration end point is reached.

6.2 Using the 10 µl syringe (5.6), add exactly 10 µl of distilled water to the contents of the cell (5.4) (with the syringe needle below the surface of the absorbent solution titrate to the zero position and note the volume of reagent used. Once again, shake the cell several times and if the electrometer needle shifts, titrate back to zero. Ignore this additional volume of Karl Fischer reagent; it represents any water which may have entered the cell as vapour while the 10 µl of water was being added.

6.3 Add a further 10 µl of water to the cell, and again titrate to the zero position. Take an average of the two titrations. If the variation is greater than 2 %, discard the contents of the cell. Introduce a further portion of absorbent solution into the cell and repeat the standardization procedure. If the titration for two further 10 µl portions of distilled water still varies by more than 2 % it is likely that the Karl Fischer reagent has aged and needs replacing with fresh reagent.

Check the delivery of the 10 µl syringe by weighing it, using a balance capable of weighing to ± 0,1 mg. Ensure that the weighings are within 1 %.

6.4 Calculate the water equivalent T, expressed in milligrams of water per millilitre, of the Karl Fischer reagent using the equation

$$T = \frac{m}{V}$$

where

m is the mass, en milligrams, of water added;

V is the volume, in millilitres, of Karl Fischer reagent required for the titration of the added water.

7 Sampling

See ISO 10101-1:1993, clause 5.

8 Procedure

NOTES

9 The apparatus may be used in the laboratory, or outside on the processing plant, with appropriate precautions. The differences between these approaches are described in 8.3. Because of the difficulty of sampling gas streams without altering their water content, the equipment is likely to be used more frequently outside the laboratory.

10 Whether it is made inside or outside the laboratory, the first determination is likely to be erroneous, due to the uncertainties associated with connecting the sample stream and purging the sampling lines. For this reason, repeat determinations are necessary on a sample stream flowing continuously at 1 l/min.

8.1 Remove the contents of the cell (5.4) and add 20 ml of the absorbent solution (4.2) to the titration cell using a dry syringe (5.5). If necessary, add sufficient water until the meter shows an excess of water and titrate back to zero with Karl Fischer reagent (4.1).

8.2 Close the gas inlet socket with a 7/16 ground glass stopper, and the gas outlet with a 5/13 ground glass stopper. Shake the cell several times so that all the internal surfaces are "wetted" and again adjust to the zero position by adding more reagent. Repeat this procedure until the needle remains steady at the zero position.

8.3 Subclauses 8.3.1 and 8.3.2 refer to the use of the equipment in the laboratory, or on the plant, respectively.

8.3.1 Switch off the stirrer and proceed to 8.4. If the sample is being taken from a line which is continuously purged, the time of purging indicated in 8.4 can be reduced.

8.3.2 In the laboratory, disconnect the apparatus from the mains supply, switch to battery operation and check that the batteries are satisfactory. Turn off the stirrer and ensure that the switch it set to "READ". The apparatus is now ready to take onto the plant.

WARNING — The equipment is neither flameproof nor intrinsically safe. Local safety regulations must be taken into account when using the equipment in hazardous zones. As a minimum

precaution, a test for flammable gases should be made in the area in which it is to be used.

8.4 Open the sampling point valve and purge the line for 5 mm at about 10 l/min. Connect the wet-test gas meter (5.2) to the sample point and adjust the flow to the required flow rate (1 l/min for streams containing less than 50 mgH_2O/m^3). Allow to purge for a further 30 min.

8.5 Disconnect the wet-test gas meter and connect the gas inlet tube of the cell to the sample point, using a metal coupling (with polychloroprene "O" rings) that is capable of connecting glass to glass or metal to glass.

NOTE 11 Under no circumstances should lengths of PVC or similar types of tubing be used to connect the sample point to the cell. This type of tubing will allow diffusion of water into the sample.

8.6 Connect the outlet of the calcium chloride guard tube (5.3) to the wet-test gas meter and the inlet to the cell outlet.

NOTE 12 Pliable tubing may be used for the connection.

8.7 Connect the cell to the gas stream by inserting the gas inlet tube through the 7/16 conical joint and allow the gas to pass through the cell for 5 min, adding reagent as necessary to maintain the cell contents at the meter zero position.

8.8 Record the wet-test gas meter reading at a convenient moment when the voltmeter reading is on zero. Record the burette reading (to the nearest 0,002 ml près) associated with this volume of gas. This first titration can be ignored, as the result is very likely to be erroneous.

8.9 Without interruption to the flow, pass an additional volume of sample (10 litres in the case of gases containing less than 50 mgH_2O/m^3), through the cell, once again adding reagent to maintain the voltmeter at or near the zero position throughout the titration. Record the wet-test gas meter reading at a moment when the voltmeter is on zero, and the corresponding burette reading (to the nearest 0,002 ml). Record the temperature and pressure of the gas in the wet-test gas meter.

8.10 Repeat the procedure described in 8.9 as many times as is necessary to obtain a constant reading (a minimum of four titrations).

9 Expression of results

9.1 Method of calculation

Calculate the water content $\varrho(H_2O)$, expressed in milligrams per cubic meter at 273,15 K (0 °C) and 101,325 kPa (1 atm), of the gas using the equation

$$\varrho(H_2O) = \frac{VT \times 1\,000(273{,}15 + \theta_A) \times 101{,}325}{V_A(p_A - p_W) \times 273{,}15}$$

where

V is the volume, in millilitres, of reagent required;

T is the water equivalent, in milligrams of water per millilitre, of the Karl Fischer reagent, calculated in 6.4;

θ_A is the temperature, in degrees Celsius, of the gas in the wet-test gas meter;

V_A is the volume, in litres, of gas passed through the cell;

p_A is the absolute pressure, in kilopascals, of the gas in the wet-test gas meter;

p_W is the vapour pressure, in kilopascals, of water at temperature θ_A.

If necessary, the observed water content can be corrected for interferences due to sulfur compounds as described in ISO 10101-1:1993, clause 4.

9.2 Precision

The precision of this method has not yet been established by an interlaboratory correlation programme.

10 Test report

The test report shall contain at least the following information:

a) a reference to this part of ISO 10101;

b) the date and time of sampling or measurement;

c) the place of sampling or measurement;

d) whether the analysis was performed on-site, or on a sample returned to the laboratory;

e) the temperature and pressure of the gas stream at the time of sampling or analysis;

f) the concentration of, and correction for, any interfering substances in the gas;

g) any deviation from the procedure specified.

Annex A
(normative)

Karl Fischer apparatus

The apparatus is shown in figures A.1 and A.2 and consists essentially of the following.

A.1 Burette

The burette is a piston-type of capacity 5 ml with a two-way PTFE key, which is attached to the base of the apparatus. The burette scale is subdivided every 0,005 ml. It is possible to estimate the burette reading to the nearest 0,002 ml. A suitable automatic burette, the performance of which is at least as good as this, may be used.

A.2 Reservoir

This is a modified 250 ml Durand bottle protected by a drying tube as shown in figure A.2. The connection between the reservoir and the burette is a butt-joint, sealed with neoprene tubing.

A.3 Titration cell

This cell is fitted with two 7/16 ground glass conical joints for the gas inlet tube and the reagent delivery tube, a 5/13 ground glass conical joint for the gas outlet and a screwed connector for the electrode. If required, a further connection can be made, at an angle on the side of the cell, for a septum.

The ground glass connectors are not lubricated (the seal is made by the reagent as the cell is shaken to wet the internal surfaces). The gas inlet tube has an internal diameter of 2,5 mm and extends to within 5 mm of the cell base. The flexible lead from the burette is drawn to a fine jet, of 0,2 mm internal diameter, to prevent diffusion of the reagent into the cell.

NOTE 13 A flexible polyethylene burette lead is necessary so that the cell can be shaken without disturbing any connections. During the normal duration of use, diffusion of moisture through the tubing is negligible. If the reagent is left in the tubing for some time, it should be flushed out thoroughly before use.

A.4 Base

The base of the apparatus contains the electronic circuits of which a diagram is shown in figure A.3 and a magnetic stirrer.

NOTES

14 The electronics function as follows.

When an excess of water is present, the electrodes are polarized and the impedence across them becomes of the same order as the 1 MΩ resistor. The voltmeter thus indicates about 0,5 V. When an excess of Karl Fischer reagent is present, the electrodes are depolarized and the impedence across them becomes very small compared with the 1 MΩ resistor. The voltmeter will now indicate 0 V. This circuit gives a very much sharper end-point indication than the more usual current measuring circuits.

15 Experience has shown that it is necessary to use a magnetic stirring bar of 20 mm to 25 mm length, to ensure adequate mixing of the cell contents.

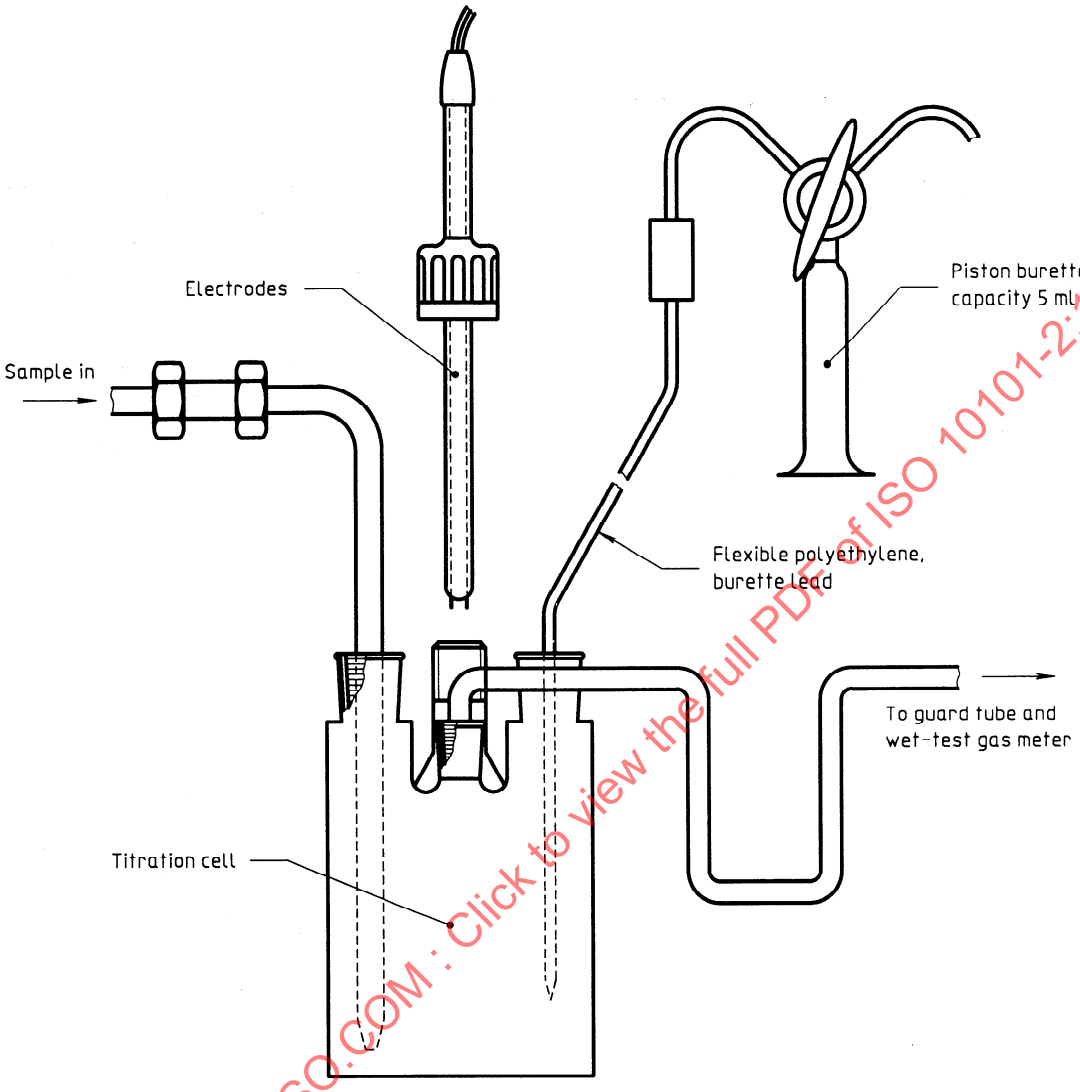

Figure A.1 — Detail of titration cell

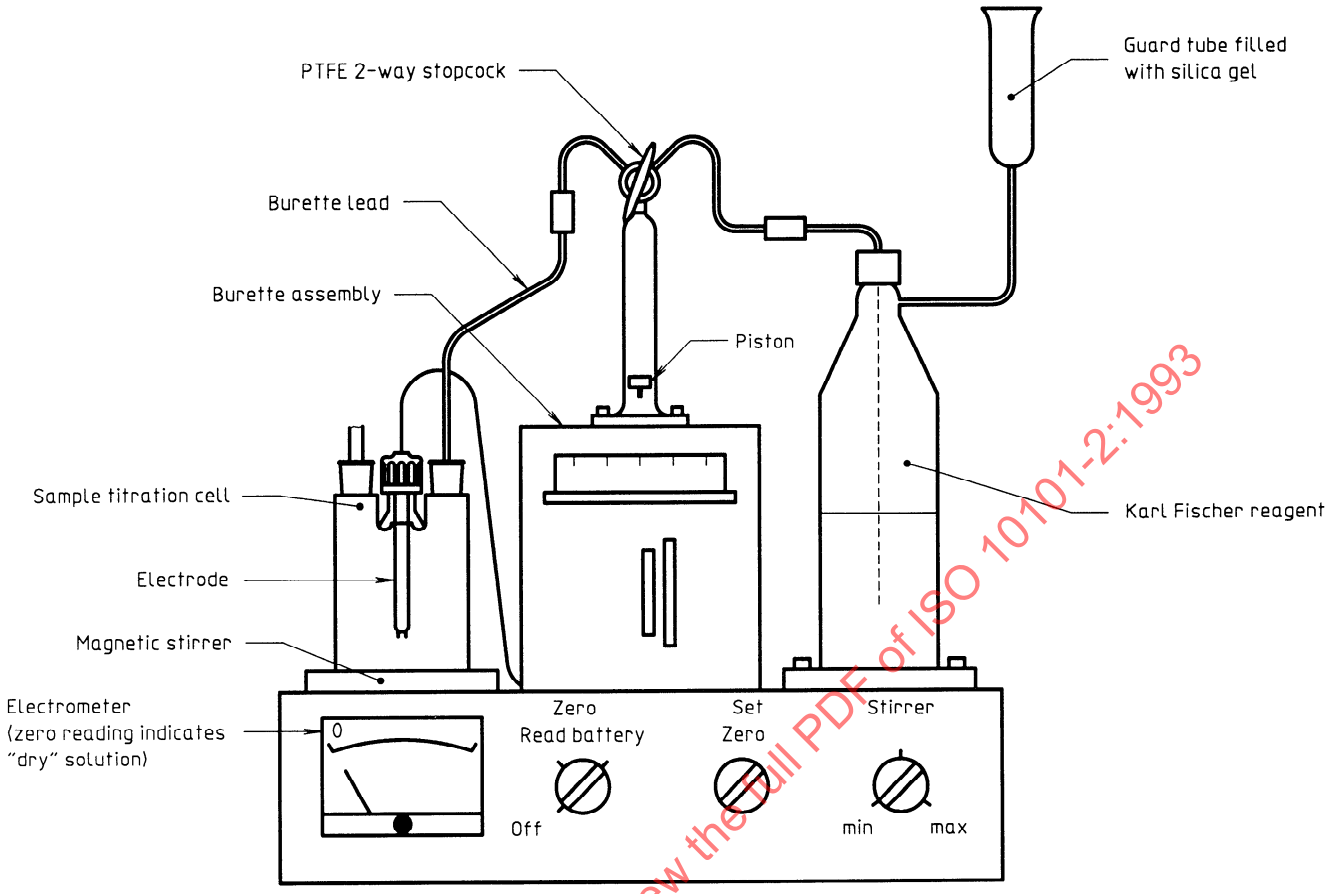

Figure A.2 — Titration apparatus — Typical assembly

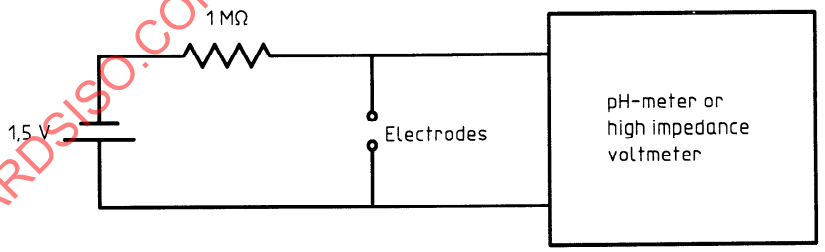

Figure A.3 — Schematic circuit diagram