

**BRITISH STANDARD METHODS FOR THE
DETERMINATION
OF WATER
(KARL FISCHER METHOD)**

BS 2511 : 1970

Confirmed
January 2011

THIS BRITISH STANDARD, having been approved by the Chemical Industry Standards Committee, was published under the authority of the Executive Board on 30 April, 1970.

First published, October 1954.

First revised, April 1970.

SBN: 580 05638 4

The Institution desires to call attention to the fact that this British Standard does not purport to include all the necessary provisions of a contract.

In order to keep abreast of progress in the industries concerned, British Standards are subject to periodical review. Suggestions for improvements will be recorded and in due course brought to the notice of the committees charged with the revision of the standards to which they refer.

A complete list of British Standards, numbering over 5000, fully indexed and with a note of the contents of each, will be found in the British Standards Yearbook, price £1. The BS Yearbook may be consulted in many public libraries and similar institutions.

This standard makes reference to the following British Standards:

BS 506. Methanol.

BS 846. Burettes and bulb burettes.

BS 1428. Microchemical apparatus:

Part D1. Burettes with pressure-filling device and automatic zero.

BS 1583. One-mark pipettes.

BS 1792. One-mark volumetric flasks.

British Standards are revised, when necessary, by the issue either of amendment slips or of revised editions. It is important that users of British Standards should ascertain that they are in possession of the latest amendments or editions.

The following BSI references relate to the work on this standard:
Committee references CIC/4 and CIC/4/-/1
Draft for comment 68/728

CONTENTS

Co-operating organizations	Page 4
Foreword	5

METHODS

1. Scope	7
2. Double burette method using an electrometric end point	7
3. Single burette method using an electrometric end point	15
4. Single burette method using a visual end point	19
5. Determination of water in ketones	22
6. Determination of microgramme quantities of water	24

APPENDIX

A. Notes on sampling for the determination of low water contents	34
--	----

FIGURES

1. Suggested alternative forms of reaction vessel	8
2. Series circuit for double burette apparatus	9
3. Mains operated shunt circuit for double burette apparatus	9
4. Apparatus for single burette system using an electrometric end point	16
5. Apparatus for single burette system using a visual end point	20
6. General assembly (showing microburette)	26
7. Detail of titration vessel (alternative design)	27
8. Electrical circuit	28
9. Dry-box assembly	29
10. Automated assembly	30
11. Sampling apparatus	30

CO-OPERATING ORGANIZATIONS

The Chemicals Industry Standards Committee, under whose supervision this British Standard was prepared, consists of representatives from the following Government departments and industrial organizations:

Board of Trade

British Steel Industry

*Chemical Industries Association

Department of Health and Social Security

Fertiliser Manufacturers' Association

Gas Council

Institution of Gas Engineers

Ministry of Agriculture, Fisheries and Food

Ministry of Technology—Laboratory of the Government Chemist

National Sulphuric Acid Association

Royal Institute of Public Health and Hygiene

The industrial organization marked with an asterisk in the above list, together with the following, was directly represented on the committee entrusted with the preparation of this British Standard:

British Laboratory Ware Association

British Plastics Federation

Ministry of Defence, Navy Department

Oil and Colour Chemists' Association

Pharmaceutical Society of Great Britain

Research Association of British Paint, Colour and Varnish Manufacturers

Royal Institute of Chemistry

Society of Motor Manufacturers and Traders Ltd.

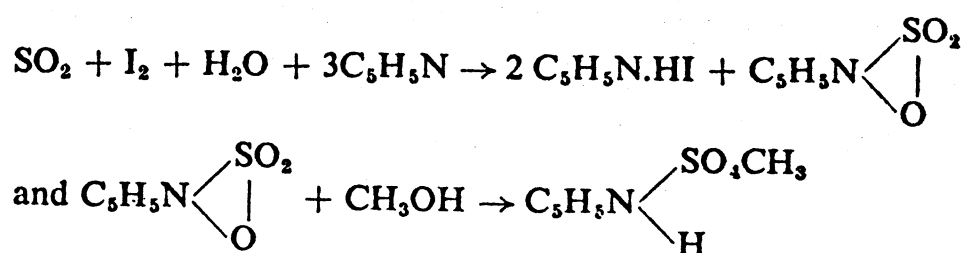
BRITISH STANDARD METHODS FOR THE DETERMINATION OF WATER (KARL FISCHER METHOD)

FOREWORD

Small quantities of water in various substances may be determined chemically by the Karl Fischer method, this method being of particular value where the common physical methods are inapplicable, especially for the determination of small percentages of water in certain liquids and in certain volatile solids.

The method is based on the reaction of water with iodine and sulphur dioxide in pyridine/methanol solution (hereinafter referred to as Fischer reagent)*. The pyridine serves to prevent loss of sulphur dioxide from the reagent by uniting with it to form an additive compound, and also facilitates completion of the reaction with water by combining with the reaction products. Ethanol may be used as the solvent, but methanol is generally preferred.

The course of the reaction in its simplest form may be expressed as follows†:



Although, according to this formula, one molecule of iodine should be equivalent to one molecule of water, in practice this stoichiometric ratio is not attained and Fischer reagent must be standardized against a known mass of water.

The end point of the titration may be determined visually by the appearance of a brown colour when excess of iodine is present. Alternatively, an electrometric procedure may be employed where the colour of the material under test renders the visual end point difficult to determine accurately. For very low water contents the electrometric procedure utilizing the 'dead stop' end point technique‡ also has the advantage of greater accuracy, even in colourless solutions.

On account of the extreme hygroscopicity of Fischer reagent, precautions must be taken to exclude all atmospheric moisture during the preparation, storage and use of the reagent.

* Karl Fischer, *Angew. Chem.*, 1935, 48, 394.

† D. M. Smith, W. M. D. Bryant and J. Mitchell, Jr., *J. Amer. Chem. Soc.*, 1939, 61, 2407.

‡ C. W. Foulk and A. T. Bawden, *J. Amer. Chem. Soc.*, 1926, 48, 2045.

In this British Standard instructions are given for the preparation of Fischer reagent, its standardization and its application to the determination of water in a variety of substances. In this revision the opportunity has been taken to amend the text of the existing clauses editorially to bring the wording into line with current conventions, but the only new material is Clause 6.

In Clause 2 details are given for the determination of water of the order of 0.02–0.5 %, in liquids and in solids capable of solution in methanol or in other suitable solvents, using the electrometric ‘dead stop’ procedure.

In Clause 3 details are given for the determination of water of up to 0.5 % by a method using more simple apparatus (single burette and electrometric end point) and giving a less accurate result.

In Clause 4 details are given of the visual method of end point detection which can be used for colourless materials where the highest degree of accuracy is not required.

Clause 5 gives details of modifications necessary for the determination of water in ketones. Two methods are given, the first involving the use of a modified reagent and the second requiring the addition of a methanol-pyridine mixture to the reaction vessel. The modified reagent is intended to give enhanced precision at very low water contents.

Clause 6 gives a method for the determination of microgramme quantities of water. The method is an extension of the Karl Fischer procedure; 1-ethyl-piperidine is used as a catalyst and constant current potentiometry is used in end point detection.

The methods described in Clauses 2, 3 and 4 are technically similar to the methods in ISO Recommendation R760, ‘Method for the determination of water by the Karl Fischer method’.

It must be appreciated that the Karl Fischer method as here described cannot be employed directly with any material which would react with any of the constituents of Fischer reagent, e.g. alkalis, metallic oxides, oxidizing agents, ketones, quinones, amines, etc. When testing materials other than those for which this method for the determination of water is quoted in British Standards, a preliminary investigation must be carried out to ascertain whether the material in question, or any normally occurring impurities therein, themselves react with the components of Fischer reagent, thereby invalidating this method for the determination of water content. It is sometimes possible, however, to obviate any such difficulties by modifications of the procedure such as:

- (1) extracting the water by means of some inert solvent,
- (2) distillation with a solvent with which water forms an azeotrope,
- (3) varying the proportions of the components of the reagent, or
- (4) preparation of derivatives which do not react with Fischer reagent.

Experience has shown that when determining the water content of some materials, erroneously low results can be obtained owing to the very slow rate of reaction between the water and the Fischer reagent. In these cases the addition

of 1-ethylpiperidine (*N*-ethylpiperidine) catalyses the reaction and accurate results can then be obtained. Addition of the catalyst in solution has been found unsatisfactory and it should be added to the reaction vessel as the pure liquid. As received, it normally contains some water and needs drying. The amount to be added varies with the material under test and should be established in each case; usually amounts of up to 1 ml are sufficient.

Examples of materials for which this addition has been found beneficial are olefine oxides and aliphatic polyhydroxy compounds with water contents less than 100 p.p.m.

In many cases the addition of the catalyst is unnecessary and it can be omitted after tests have confirmed this.

METHODS

1. SCOPE

This British Standard specifies methods for the preparation and standardization of Fischer reagent and its application to the determination of water in a variety of substances.

2. DOUBLE BURETTE METHOD USING AN ELECTROMETRIC END POINT

2.1 General. This method is intended for use where the highest degree of accuracy is required and is suitable for the determination of water in organic solvents and similar materials having water contents of the order of 0.1 %. At this level the maximum deviation from the mean of results obtained in different laboratories will not normally exceed 0.01 % of water.

2.2 Apparatus. Complete sets of apparatus for determination of water by the Karl Fischer method are available from the trade. These are of different types designed to meet different requirements as to sensitivity and accuracy. In order to avoid unnecessary restriction the apparatus is described in general terms, except where strict adherence to a particular type or size is considered essential.

(1) *Reaction vessel.* The reaction vessel (see Fig. 1) has a working capacity of not less than 60 ml. The wide neck has an airtight detachable head fitted to accommodate two burette jets (extended to suitable length) and tubes for entry and exit of nitrogen. An additional hole, protected by a suitable seal, accommodates the spindle of a stirrer (unless magnetic stirring is provided). Two platinum wire electrodes extending nearly to the bottom of the vessel are either fused in through the side of the vessel or inserted through the head, if preferred. A drain cock is provided. A side tube, closed by a translucent latex vaccine cap, provides for insertion of liquid samples without exposing the contents of the vessel to atmospheric moisture during the operation.

NOTE. Care should be taken in the construction of the vessel to avoid excessive 'dead space' in the region of the drain cock.

(2) *Two burettes.* The two burettes are of 25 ml capacity (or other capacity

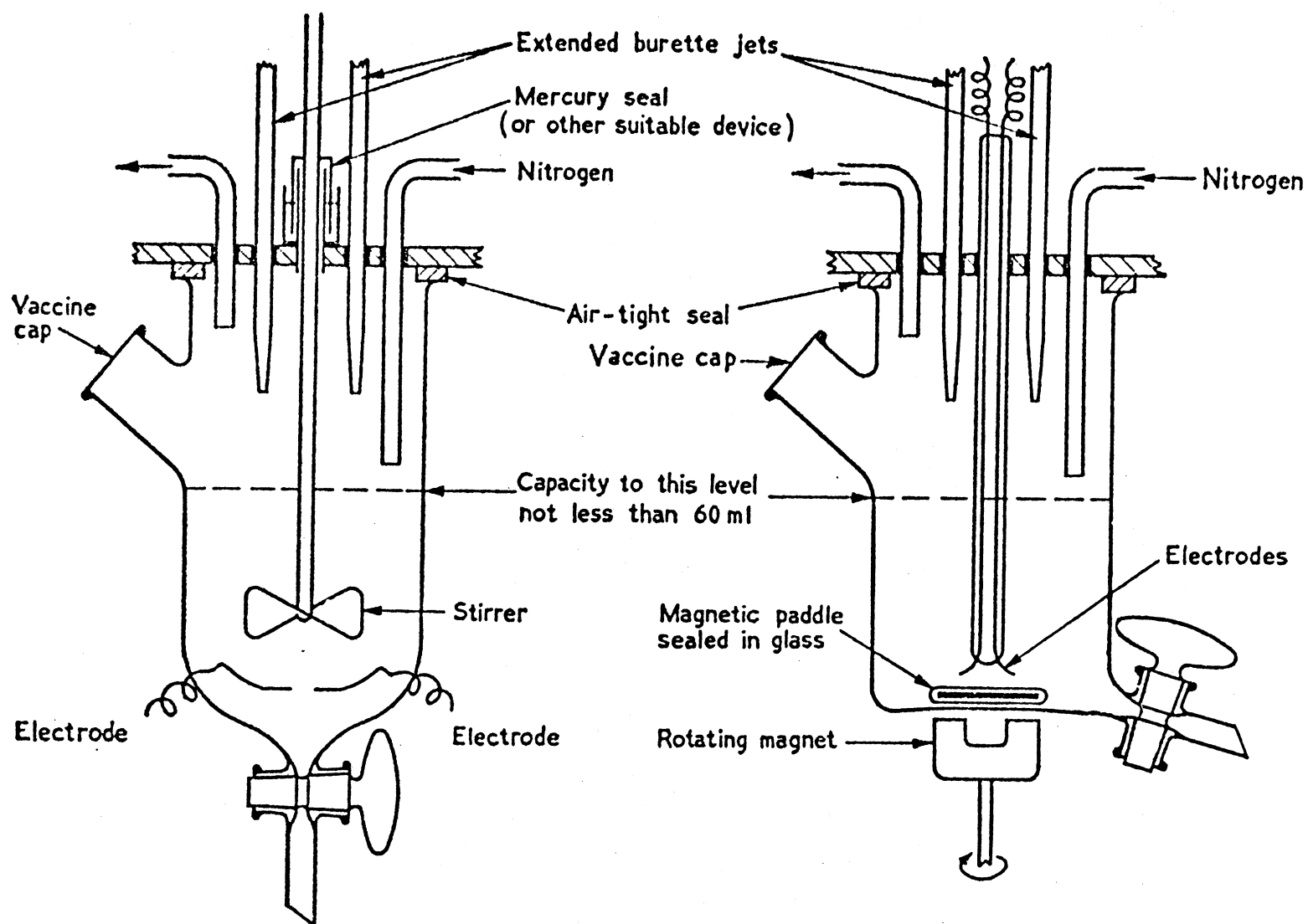


Fig. 1. Suggested alternative forms of reaction vessel

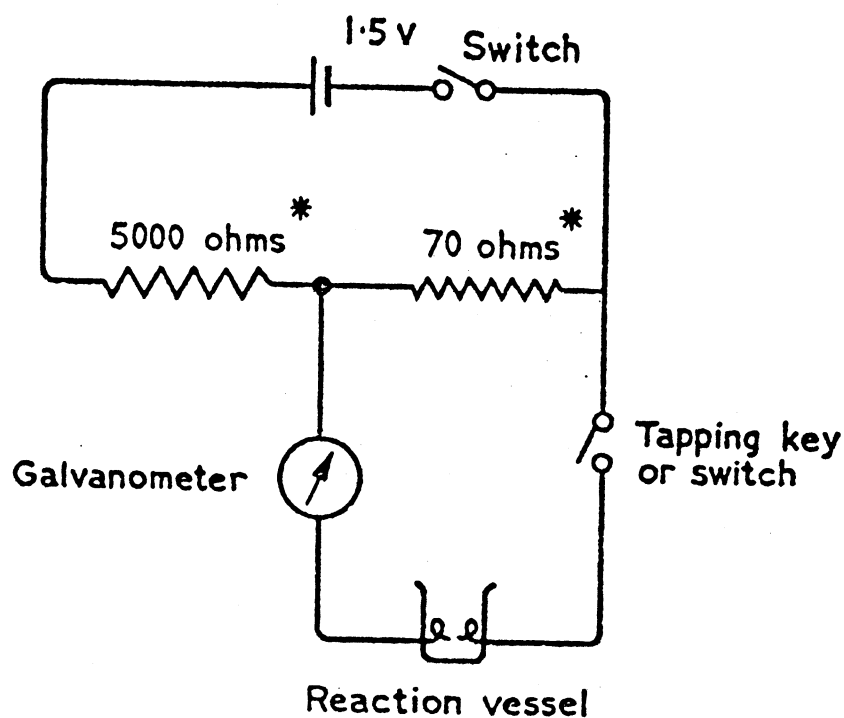


Fig. 2. Series circuit for double burette apparatus

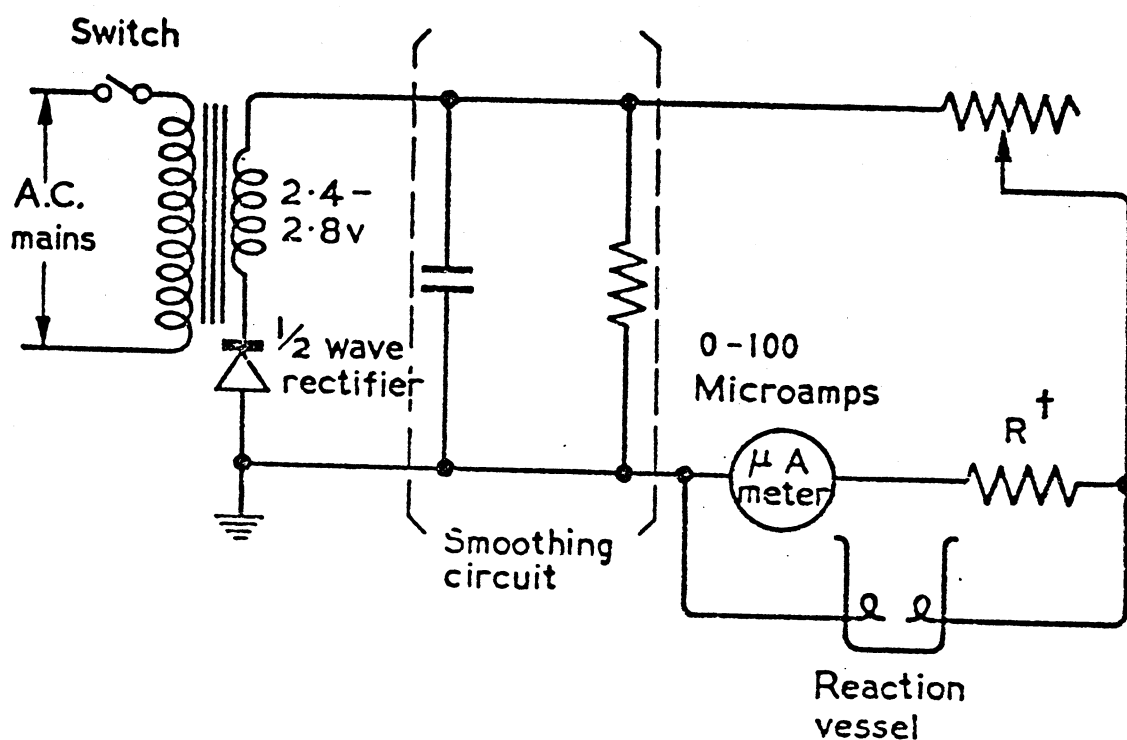


Fig. 3. Mains operated shunt circuit for double burette apparatus

* Values shown for resistances will depend to some extent on the size and distance apart of the electrodes.

† Total resistance of microammeter and resistor R in series to be approximately 4600Ω .

as preferred). When solid samples are to be examined there is a third burette of 100 ml capacity. All are Class A, complying with BS 846*.

(3) *Two reagent reservoirs*. These are suitably connected to the burettes for gravity, suction or pressure feed. Provision is made for drying the air used for blowing or displacing the reagents.

(4) *Glass stirrer*. The stirrer is either mechanically driven from above or magnetically driven from below.

(5) *Electrical equipment*. This is to provide for the application of not more than 20 mV to the electrodes when there is an excess of 0.2 ml of Fischer reagent. Suitable circuits are shown diagrammatically in Figs. 2 and 3.

(6) *Galvanometer*. This has a sensitivity such that full scale deflection is obtained by a current of not more than 100 μ A. The galvanometer may be in series with the reaction vessel or in a shunt position. In the former case the galvanometer will give a 'null' reading at the end point and in the latter case a positive reading. For use in the series position the galvanometer should have a resistance not exceeding 100 Ω .

(7) *Tapping key or switch*

(8) *Pipettes†*. Pipettes are of 10 ml and 20 ml capacity, fitted with hypodermic needles of about 1 mm bore (1.5 mm for use with the more viscous liquids such as the higher alkyl phthalates) and provided with suitable protection against atmospheric moisture.

(9) *Three additional hypodermic needles*. These are of about 1 mm bore.

(10) *Weighing pipette*. This is fitted with a hypodermic needle, of about 1 mm bore, in place of the usual jet.

(11) *Three drying bottles*. The bottles are for drying the nitrogen supply, one containing concentrated sulphuric acid and two containing freshly activated silica gel, in that order.

(12) *One-mark volumetric flasks‡*. These are of 100 ml capacity, closed with translucent latex vaccine caps.

NOTE 1. All possible points of entry of atmospheric moisture into the apparatus (including the suction end of the pipettes) are protected by guard tubes filled with freshly activated silica gel or other efficient desiccant. On safety grounds the use of granular magnesium perchlorate is not recommended.

NOTE 2. Silicon grease is used for lubrication of stopcocks. Petroleum jelly is not suitable, owing to its reactivity with Fischer reagent.

2.3 Reagents. The following reagents are required:

(1) *Methanol*, complying with BS 506§ and dried as described in 2.4, or anhydrous methanol denatured with pyridine.

(2) *Nitrogen*, from a cylinder of compressed gas.

(3) *Fischer reagent*, having a water equivalent of 3.0–4.0 mg/ml. This may be prepared as described in 2.4 from the methanol and:

* BS 846, 'Burettes and bulb burettes'.

† Pipettes complying with BS 1583, 'One-mark pipettes', Class A, are suitable.

‡ Flasks complying with BS 1792, 'One-mark volumetric flasks', are suitable.

§ BS 506, 'Methanol'.

- (i) pyridine, laboratory reagent quality;
- (ii) iodine, resublimed;
- (iii) sulphur dioxide, liquid, refrigeration grade, from a glass siphon.

NOTE. This strength of reagent has been found generally convenient for determining percentages of water of the order of 0.1 %, using the apparatus and procedure detailed, but any other strength of reagent between about 2.5 mg/ml and 5.0 mg/ml may be adopted if preferred.

(4) *1-ethylpiperidine* (*N*-ethylpiperidine), dried over silica gel or a molecular sieve.

2.4 Preparation of reagents. Prepare reagents by the following methods:

(1) *Methanol*. Dry methanol, if it is not already anhydrous, by distillation over magnesium turnings and a little iodine, or by fractionation through a 1.6 mm rectifying column, and distil it into a receiver protected from atmospheric moisture by a guard tube. Methanol dried in this manner will contain not more than 0.03 % of water.

(2) *Water/methanol*. To approximately 900 ml of the methanol in a 1 litre one-mark volumetric flask add 1.5 ml of distilled water. Make up to the mark with the methanol, mix thoroughly and transfer to the appropriate burette reservoir.

(3) *Pyridine*. Distil the pyridine, collecting the fraction boiling between 114 °C and 116 °C at 101.3kN/m²* (760 mmHg) pressure, the receiver being protected from atmospheric moisture by a guard tube.

(4) *Fischer reagent*. Measure 800 ml of the methanol into a dry 1500 ml glass-stoppered flask. Add 160 g of pyridine. Exchange the glass stopper for a two hole rubber stopper fitted with an inlet tube reaching nearly to the bottom of the flask and a short outlet tube protected by a guard tube. Weigh the flask with its fittings and contents and cool in ice water. Connect the inlet tube to the siphon of sulphur dioxide and allow the gas to pass into the mixture with continuous agitation until the total mass of the flask and its contents is increased by about 40 g. Then remove the rubber stopper and delivery tubes and add 90 g of iodine. Replace the glass stopper, shake to dissolve the iodine and allow the mixture to stand for 24 h. Finally, transfer the prepared reagent to the appropriate burette reservoir bottle. The water equivalent of the Fischer reagent thus prepared will be about 3.5 mg/ml.

2.5 Procedure

2.5.1 Standardization of the water/methanol reagent. Run into the reaction vessel enough Fischer reagent to cover the electrodes. Switch on the stirrer and turn on a slow stream of nitrogen. When a series of tests begins, leave the apparatus with the stirrer running for about 15 min to allow all traces of water to be removed. (Continue the passage of nitrogen and the stirring throughout the

* 1kN/m² = 10 mbar = 7.5 mmHg.