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Liquid chlorine for industrial use — Determination of water content using an electrolytic analyser

ADDENDUM 1

Addendum 1 to International Standard ISO 2202 was drawn up by Technical Committee ISO/TC 47, *Chemistry*, and circulated to the Member Bodies in November 1973.

It has been approved by the Member Bodies of the following countries :

Austria
Belgium
Bulgaria
Chile
Czechoslovakia
Egypt, Arab Rep. of
Finland
France
Germany
Hungary
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Korea, Rep. of
Netherlands
Portugal
South Africa, Rep. of
Spain
Switzerland
Thailand
Turkey
United Kingdom
U.S.S.R.

No Member Body expressed disapproval of the document.

1 SCOPE AND FIELD OF APPLICATION

This addendum to ISO 2202 specifies a simple and rapid procedure for checking the ageing of the electrolytic cell used for the determination of water in liquid chlorine with an electrolytic analyzer. It can advantageously replace the rather long procedure described in 6.3 of ISO 2202, which necessitates the preparation of gases of known water content in an apparatus of delicate construction. In addition, this procedure makes it possible to calculate rapidly the output of the cell, the working life of which can thus be extended until the output falls to 75 % or even less before the cell need be replaced or regenerated.

2 REFERENCES

ISO/R 760, *Determination of water by the Karl Fischer method.*

ISO 2120, *Liquid chlorine for industrial use — Determination of the content of chlorine by volume in the vaporized product.*

3 PRINCIPLE

Injection into the gas to be analyzed of a known volume of solvent, the water content of which has been determined by the Karl Fischer method.

Measurement, after approximately 15 min, of the area of the peak appearing on the recorder chart.

Calculation of the output of the electrolytic cell by relating the number of coulombs corresponding to this area to the theoretical number of coulombs required to electrolyze the quantity of water injected.

4 REAGENTS

4.1 Solvent of known water content

Use a chlorinated solvent such as 1,2-dichloroethane, for example, which has a water content of about 1 g/l. Determine the water content by the Karl Fischer method specified in ISO/R 760.

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Descriptors : chlorine, liquefied gases, chemical analysis, electrolytic analysis, moisture content.

Price based on 5 pages

5 APPARATUS

Use the apparatus shown in diagrammatic form in figure 1. This apparatus comprises the same components as those described in 5.5 to 5.11 of ISO 2202. In addition, it includes the following components :

5.1 Syringe (S), 100 μl, containing the solvent (4.1), fitted with a needle (L_1) of internal diameter 0,18 mm, for injecting the solvent into the gas being analyzed.

5.2 Injection chamber (J), (T-tube), into which the solvent of known water content is injected for the check test.

5.3 Flexible septum (M), silicone-based, resistant to chlorine and free from water, pierced by the needle L_1. This septum is placed over the opening of the injection chamber (lateral part of the T-tube) and is held in position by a washer and screw cap.

5.4 Recorder (P), for the continuous measurement of the electrolysis current.

Figure 2 shows the apparatus used for drawing off the solvent (4.1), which comprises :

5.5 Two-necked flask (B), approximately 100 ml capacity, one neck fitted with a ground glass stopper and the other with a T-bore stopcock (R_7) through which the needle (L_2) passes from the syringe (S), enabling the solvent to be drawn off under a flow of dry nitrogen introduced through the side tube of the stopcock (R_7).

5.6 Needle (L_2), of internal diameter 0,30 mm, used for filling the syringe (S).

6 PROCEDURE

Assemble the apparatus, put it into operation and carry out the determinations according to the instructions given in clause 6 of ISO 2202. Make the connection to the vaporized chlorine at a point where it is not under pressure (behind the valve (C), in the case of the diagram shown in ISO 2120). To check the analyzer, ensure that the water content of the gas to be analyzed, read on the recorder, remains stable for at least 15 min. Then fill the syringe (S) as follows.

Detach the syringe from the needle (L_1) without withdrawing the latter from the septum (M) and attach the syringe to the needle (L_2). Place this needle in the flask (B), containing the solvent, through the stopcock (R_7). During this operation, pass a current of dry nitrogen through the stopcock (R_7) so as to prevent the ingress of moisture.

Rinse the syringe three times with fresh solvent (4.1), then fill it and attach it again to the needle (L_1). Rinse this needle by injecting a preliminary volume of about 10 μl of the solvent into the injection chamber (J) and wait until the water content read on the recorder returns to its original value.

Then place a suitable volume of the solvent (4.1) in the injection chamber for the blank test (usually 20 μl when its water content is of the order of 1 g/l, corresponding to 20 μg of water).

Wait until the recorder reading has returned practically to its initial value, which is generally after about 15 min.

Calculate the output of the electrolytic cell from the graph obtained, as indicated in clause 7. A typical graph is shown in figure 3.

In practice, it is possible to extend the working life of electrolytic cells, which undergo slow and regular reduction in sensitivity until their output has dropped to 75 % or less, before it is necessary to regenerate or replace them.

7 EXPRESSION OF RESULTS

7.1 The performance, R, of the electrolytic cell, expressed as a percentage, is given by the formula

$$R = 100 \times \frac{C_1}{C}$$

where C and C_1 respectively represent the number of coulombs required theoretically and in practice for the electrolysis of the quantity of water injected.

These values of C and C_1 are calculated as shown in 7.2 and 7.3.

7.2 $C = 96{,}5 \times \frac{m}{9{,}008}$

where

96,5 is the number of coulombs corresponding to 1 milligram-equivalent of water;

9,008 is the mass, in milligrams, of 1 milligram-equivalent of water;

m is the mass, in milligrams, of water contained in the injected volume of solvent (4.1).

7.3 $C_1 = I \times t \times \frac{S_1}{S}$

where

I is the current, in amperes, corresponding to the highest reading of the recorder scale (0,002 A in the example shown in figure 3);

t is the time, in seconds, of the recording;

$\frac{S_1}{S}$ is the ratio of the area of the recorder peak (shaded area of figure 3) to the total area of the rectangle $I \times t$. This ratio can be determined by calculation, by weighing the cut out areas, or by any other means.

Example of calculation relating to the diagram shown in figure 3 :

m = 0,020 mg of H_2O

S_1 = 0,246 g

S = 2,478 g

I = 0,002 A

t = 15 × 60 = 900 s

Calculation of C : $96{,}5 \times \frac{0{,}020}{9{,}008} = 0{,}214\,2$ coulomb

Calculation of C_1 : $0{,}002 \times 900 \times \frac{0{,}246}{2{,}478} = 0{,}178\,6$ coulomb

Performance of the electrolytic cell :

$$R = 100 \times \frac{0{,}178\,6}{0{,}214\,2} = 83{,}3\ \%$$

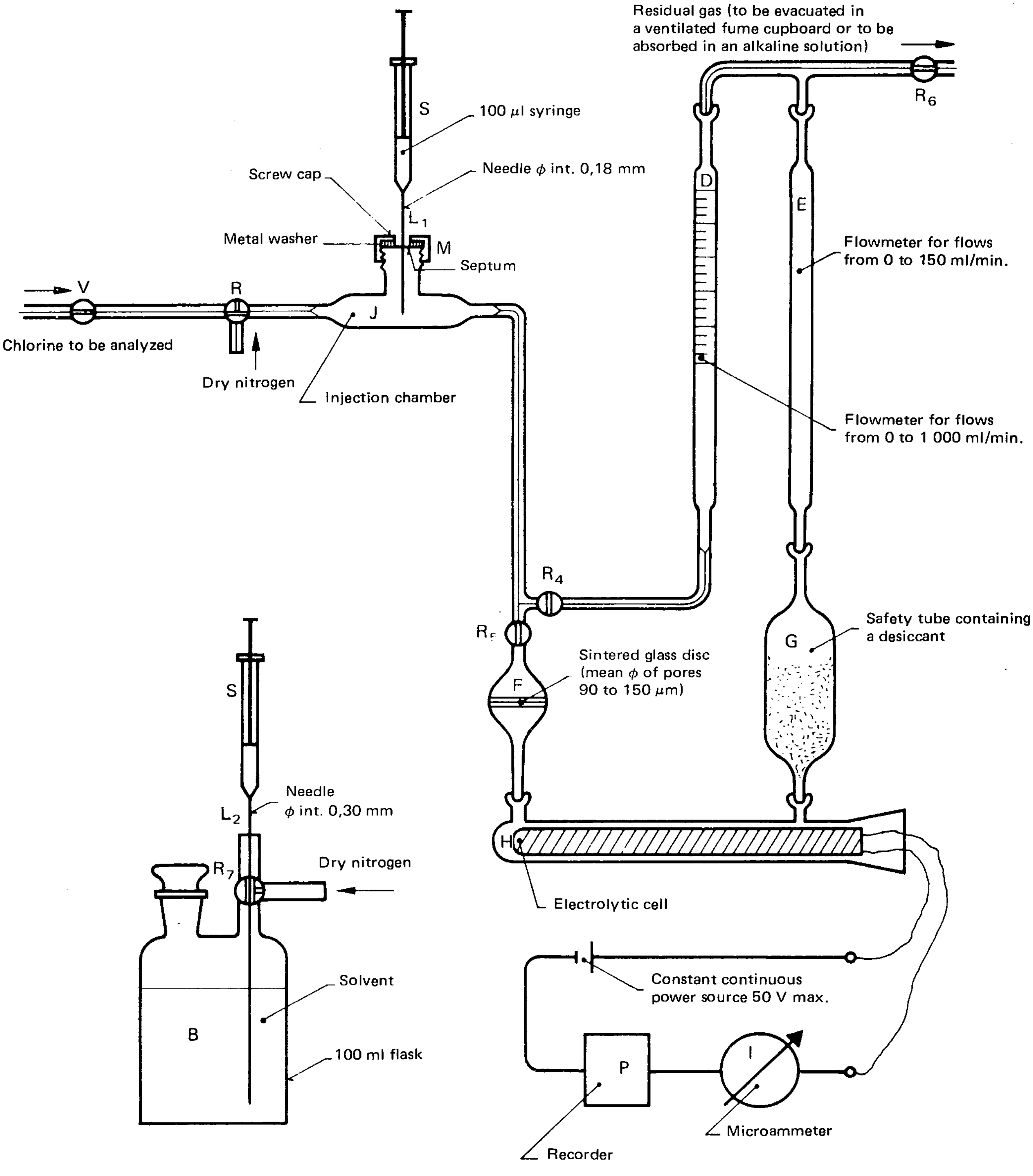

FIGURE 2 – **Device for drawing off solvent**

FIGURE 1 – **Diagram of an electrolytic analyzer and the control device**

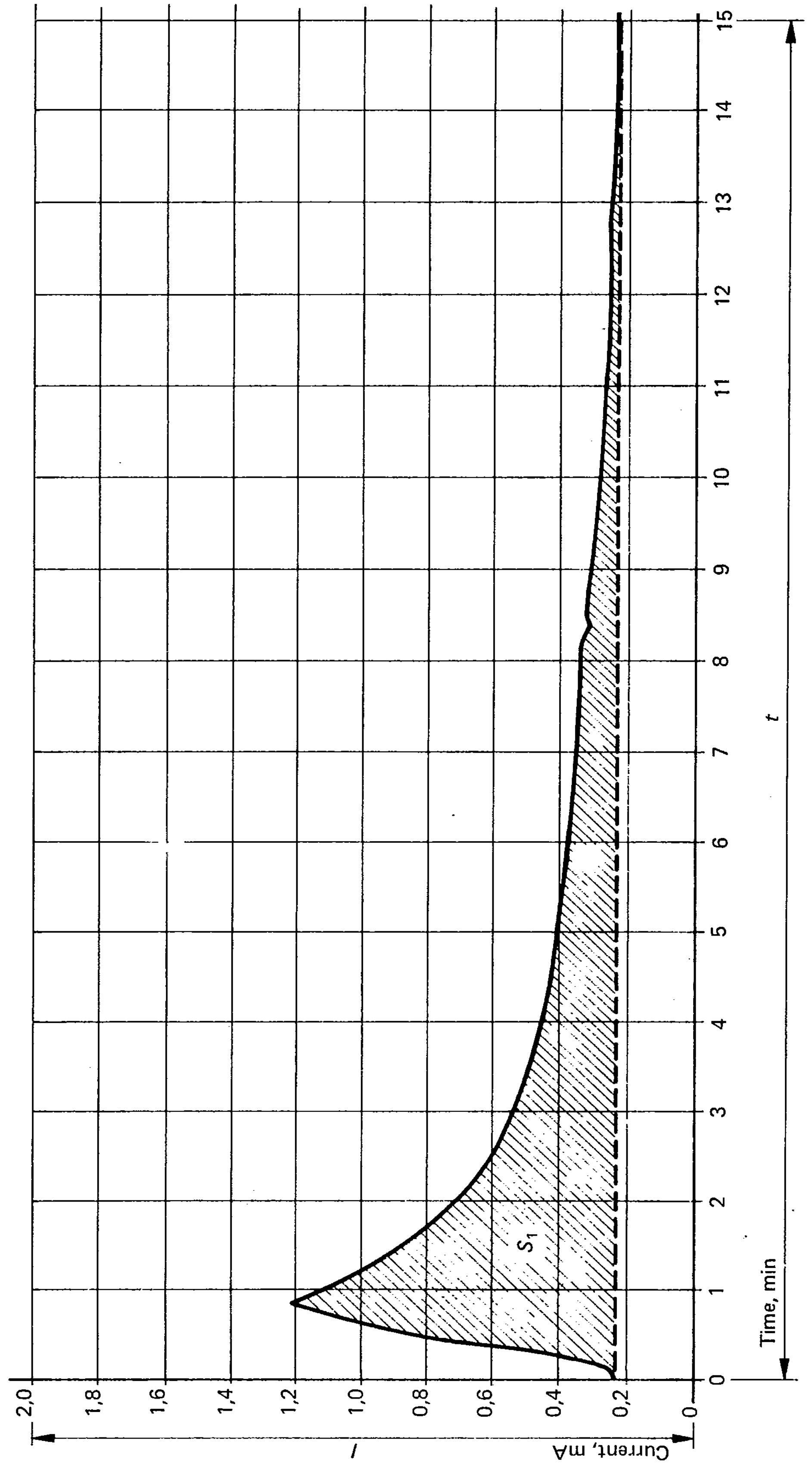

FIGURE 3 – Typical graph

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INTERNATIONAL STANDARD ISO 2202

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Liquid chlorine for industrial use — Determination of water content using an electrolytic analyser

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up 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.

Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 2202 was drawn up by Technical Committee ISO/TC 47, *Chemistry.*

It was approved in May 1971 by the Member Bodies of the following countries:

Austria
Belgium
Bulgaria
Chile
Egypt, Arab Rep. of
France
Germany
Hungary
India
Israel
Italy
Netherlands
New Zealand
Portugal
Romania
South Africa, Rep. of
Sweden
Switzerland
Turkey
United Kingdom
U.S.A.
U.S.S.R.

The Member Body of the following country expressed disapproval of the document on technical grounds:

Poland

Printed in Switzerland

Liquid chlorine for industrial use — Determination of water content using an electrolytic analyser

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method for the determination of the volatile water, i.e. that which volatilizes at the same time as the chlorine, originating from the gasification of liquid chlorine for industrial use.

This method is intended for products with a volatile water content of at least 10 ppm (0.001 % V/V).

2 REFERENCE

ISO/R 653, *Long solid-stem thermometers for precision use.*

3 PRINCIPLE

Continuous absorption of the water in the gasified chlorine, flowing at a rate of 100 ml/min over phosphorus pentoxide applied in a thin layer on a glass rod, forming an electrolytic cell by means of two electrodes (for example, platinum) wound over its entire length.

Decomposition of the water, on absorption, by electrolysis.

Measurement of the electrolytic current, which is a function of the water content.

4 REAGENTS AND MATERIALS

4.1 Sulphuric acid, ρ 1.71 g/ml, 78.5 % (m/m) solution, or any other sulphuric acid solution of known concentration between 76 and 85 % (m/m).

4.2 Desiccant, resistant to chlorine (silica gel for example).

4.3 Dry nitrogen, having a water content less than 10 ppm (V/V).

4.4 Chlorine-resistant grease

Greases based on fluorinated or chlorofluorinated products are suitable.

5 APPARATUS

Use an apparatus available commercially. A type of apparatus is shown diagramatically in Figure 1.

The gas circuit is made up of borosilicate glass semi-capillary tubes having only greased ground joints, employing the grease (4.4); or joints of fluorocarbon polymer (with no flexible connections, rubber or plastics, that can be attacked by chlorine).

This apparatus includes six glass stopcocks having bodies made of fluorocarbon polymer of the polytetrafluoroethylene type (R_1 to R_6) and a similar threeway cock R.

The components are as follows :

5.1 Bubbler (A) for checking the analyser, containing a sufficient volume of the sulphuric acid solution (4.1) to immerse all the sintered glass plates, under the conditions of use.

5.2 Thermostatic sheath (B) surrounding the bubbler.

5.3 Long solid-stem precision thermometer (T) complying with ISO/R 653, and providing a temperature reading between 15 and 30 °C accurate to ± 0.1 °C.

5.4 Safety flask (C).

5.5 Gas flow meter (D), for reading gaseous chlorine flow rates between 0 and 1 000 ml/min.

5.6 Gas flow meter (E), for reading gaseous chlorine flow rates between 0 and 150 ml/min.

5.7 Sintered glass filter (F), porosity grade P160 (pore size index 100 — 160 μm), for protecting the cell (H).

5.8 Electrolytic cell (H), comprising a borosilicate glass rod, on which two electrodes, usually platinum, are wound over the entire length and between which a film of phosphorus pentoxide is applied in a thin layer. The tube is enclosed in an envelope, also of glass, protected from external moisture by a guard tube containing a desiccant (4.2). The whole should be capable of being readily dismantled and cleaned for regenerating the cell.

5.9 Microammeter (I), with a variable scale, having a maximum sensitivity of 50 μA, corresponding to approximately 4 ppm (V/V) of water, fitted in such a way that it can be short-circuited while the cell is being dried, in order to protect it.

5.10 Constant direct voltage source (K) not exceeding 50 V. Use preferably batteries. Failing this, use a rectified a.c. power source having a peak inverse voltage of less than 40 mV.

5.11 Safety-tube (G), containing the desiccant (4.2).

NOTE — If the gas rate to be controlled is not constant, it is essential that the apparatus includes a flow regulator, or that the gas circuit includes a suitable differential pressure regulator with a stainless steel body and a fluorocarbon polymer membrane, resistant to chlorine.

6 PROCEDURE

6.1 Safety measures

PERSONNEL WORKING WITH CHLORINE SHALL BE INSTRUCTED IN THE HAZARDS OF THE PRODUCT AND THE SAFETY MEASURES TO BE OBSERVED.

CHLORINE IS A VESICATORY, IRRITANT AND SUFFOCATING GAS. THE CHLORINE CONCENTRATION IN THE ATMOSPHERE SHALL NOT EXCEED 1 ppm (V/V), OR 3 mg/m^3.

FOR THESE REASONS IT IS RECOMMENDED THAT PROTECTIVE CLOTHING AND GOGGLES BE WORN AND THAT THE WORK PLACE BE SUITABLY VENTILATED, BEARING IN MIND THAT THE GAS, WHICH IS HEAVIER THAN AIR, COLLECTS IN LOW AREAS.

IN THE CASE OF A SIGNIFICANT LEAK, ONLY PERSONNEL WEARING APPROPRIATE MASKS SHALL REMAIN IN THE CONTAMINATED AREA. THE LEAK CAN BE LOCATED BY MEANS OF A RAG SOAKED IN AMMONIA.

PERSONS POISONED BY INHALING THE GAS SHALL BE TAKEN FROM THE CONTAMINATED ZONE AS QUICKLY AS POSSIBLE, AVOIDING ALL MUSCULAR EFFORT. THEY SHALL BE KEPT QUIET, AWAY FROM COLD, AND FIRST AID SHALL BE APPLIED AS NECESSARY, WHILE AWAITING THE ARRIVAL OF THE DOCTOR. IF BREATHING CEASES, IMMEDIATELY APPLY ARTIFICIAL RESPIRATION.

6.2 Installation of the apparatus and putting it into operation

The analyser shall be installed as near as possible to the chlorine the water content of which is required, and a connection shall be made employing 2 X 6 mm fluorocarbon polymer tubes with joints of the same material. A stop valve (V) (see Figure 1) shall be fitted at the end of this line, approximately 200 mm from the analyser, in order to isolate the line, and in this way to avoid taking in moisture in the event of the apparatus failing.

First of all, completely clean all lines with water, then with acetone, in order to remove all particles that might affect the performance of the cell, subsequently drying by flushing with dry nitrogen (4.3) until the acetone is completely removed.

Next, connect up the apparatus, close the stopcocks R_1, R_3 and R_5, and open stopcocks R_2, R_4 and R_6. Connect up the cell. The voltage is not critical, but it is recommended not to exceed 50 V. Operate the stopcock R so as to admit dry nitrogen (4.3) to the analyser at a rate of 500 to 1 000 ml/min, measured on the flow meter (D).

After approximately 15 min, adjust the stopcocks R_4 and R_5 so as to pass part of the nitrogen to the electrolytic cell (H), at a rate such that the current does not exceed 10 mA. If necessary, reduce or even stop the nitrogen supply. Then regulate the flow to 100 ml/min, measured by the flow meter (E).

Wait until the ammeter (I) indicates a value corresponding to less than 10 ppm (V/V) of water, or less than 132 μA.

NOTE — During all these operations and during those described below, take care not to close R_6 before the flow of gas measured by the flow meter is exhausted.

6.3 Checking

In principle, the analyser, thus installed, does not require standardizing, since the procedure is based on the application of a physical law.

In practice some apparatuses do not give a quantitative electrolysis and it is convenient to carry out the following checking test using the chlorine being analysed after having adjusted its water content by previously bubbling through a sulphuric acid solution of known concentration and temperature.

Reduce the total gas flow rate to slightly more than 100 ml/min, measured by the flow meter (D), open stopcocks R_1 and R_3, and close R_2 so as to pass the gas into the bubbler containing the sulphuric acid solution (4.1).

Next open stopcock R_5 and partially close R_4 in order to pass exactly 100 ml/min of gas, measured by the flow meter (E) into the electrolytic cell (H).

Record the electric current after it has remained constant for at least 10 min, in addition to the temperature on the thermometer (T).

The water content obtained should be within 10 %, in relative value, of that indicated on the graph (Figure 2) for the concentration and temperature of the sulphuric acid solution (4.1) in the bubbler (A).

6.4 Determination

After the apparatus has been installed and dried as described in 6.2, close stopcocks R_1, R_3 and R_5, and open R_2, R_4 and R_6, then adjust the valve (V) and stopcock R so as to admit the chlorine to be analysed into the apparatus at a rate of 500 to 1 000 ml/min for approximately 15 min.

Cautiously open stopcock R_5, and partially close stopcock R_4, passing the chlorine to be analysed into the cell (H) at a temperature of 20 ± 2 °C and at a rate such that the current does not exceed 10 mA. If necessary, reduce or even stop the flow of chlorine at the start and pass a little dry nitrogen (4.3) into the analyser before readmitting.

Now regulate the chlorine flow rate through the cell to 100 ml/min, measured by the flow meter (E).

Record the electric current after it has remained constant for at least 10 min.

6.5 Checking the performance of the apparatus

Two sets of factors can affect performance of the phosphorus pentoxide cell.

6.5.1 Those resulting in short circuit between the electrodes, and thus putting the cell out of action.

These usually involve very fine particles of conducting material not held back by the filter (5.7) or introduced accidentally whilst setting up the apparatus.

It is then necessary to replace the cell or to clean it and to regenerate it according to the manufacturer's instructions.

6.5.2 Those resulting in slow poisoning of the phosphorus pentoxide, bringing about a gradual reduction in sensitivity, a slower response rate and faulty results.

These involve gaseous or liquid impurities entrained by the chlorine and capable of reacting with the phosphorus pentoxide or being absorbed on its surface, thus reducing the efficiency of the cell. It is therefore necessary to check the performance of the analyser from time to time, confirming the following points :

6.5.2.1 The water content observed on reducing the chlorine rate to half should be half the initial value, with a maximum relative deviation of 10 %. If the value read off is clearly greater than half, accidental entry of water into the apparatus may be involved.

6.5.2.2 The microammeter pointer should always return close to zero when the flow of chlorine is cut off for 30 min approximately, and then to within 10 % (in relative value) of its initial value, on restoring the flow.

6.5.2.3 The microammeter pointer should return to within 10 % (in relative value) of its initial value after stabilizing, when the electrolysis current has been interrupted and then restored after 3 to 5 min.

If the results of these checks are not satisfactory, the cell should be replaced or cleaned and regenerated according to the manufacturer's instructions.

7 EXPRESSION OF RESULTS

It is convenient in practice to graduate the microammeter directly in terms of parts per million of water.

Calculation of the water content, as a function of current obtained, is carried out in accordance with the following data :

96 500 coulombs correspond to 1 gram equivalent of water;

96.5 coulombs correspond to 1 milligram equivalent of water;

$96.5 \times 2 = 193$ coulombs correspond to 1 milligram molecule of water.

Hence,

1 coulomb corresponds to electrolysis of $\frac{18.016}{193} = 0.093\,3$ mg of water, or $\frac{24.3}{193} = 0.125\,8$ ml of water vapour at 20 °C and 760 mmHg.

If the chlorine is passed to the cell at a rate of 100 ml/min, or $\frac{100 \times 10^{-6}}{60}$ m^3/s, a current of 1 μA would correspond to the following water contents in the gas :

$0.125\,8 \times \frac{60}{100 \times 10^{-6}} \times 10^{-6} = 0.075\,5$ ml/m^3 or ppm (V/V);

$0.093\,3 \times \frac{60}{100 \times 10^{-6}} \times 10^{-6} = 0.056\,0$ mg/m^3;

$0.093\,3 \times \frac{60}{100 \times 10^{-6}} \times 10^{-6} \times \frac{1}{2.99} = 0.018\,7$ mg/kg or ppm (m/m).

2.99 being the density of gaseous chlorine, in kilograms per cubic metre, for the conditions of analysis, that is to say at 20 °C and 760 mmHg.

NOTE — To obtain the sensitivity of the method, note that :

1 ml/m^3 or 1 ppm (V/V) corresponds to a current of $\frac{1}{0.075\,5} = 13.24$ μA;

1 mg/m^3 corresponds to a current of $\frac{1}{0.056\,0} = 17.9$ μA;

1 mg/kg or 1 ppm (m/m) corresponds to a current of $\frac{1}{0.018\,7} = 53.5$ μA.

8 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard or regarded as optional.

Dimensions in millimetres

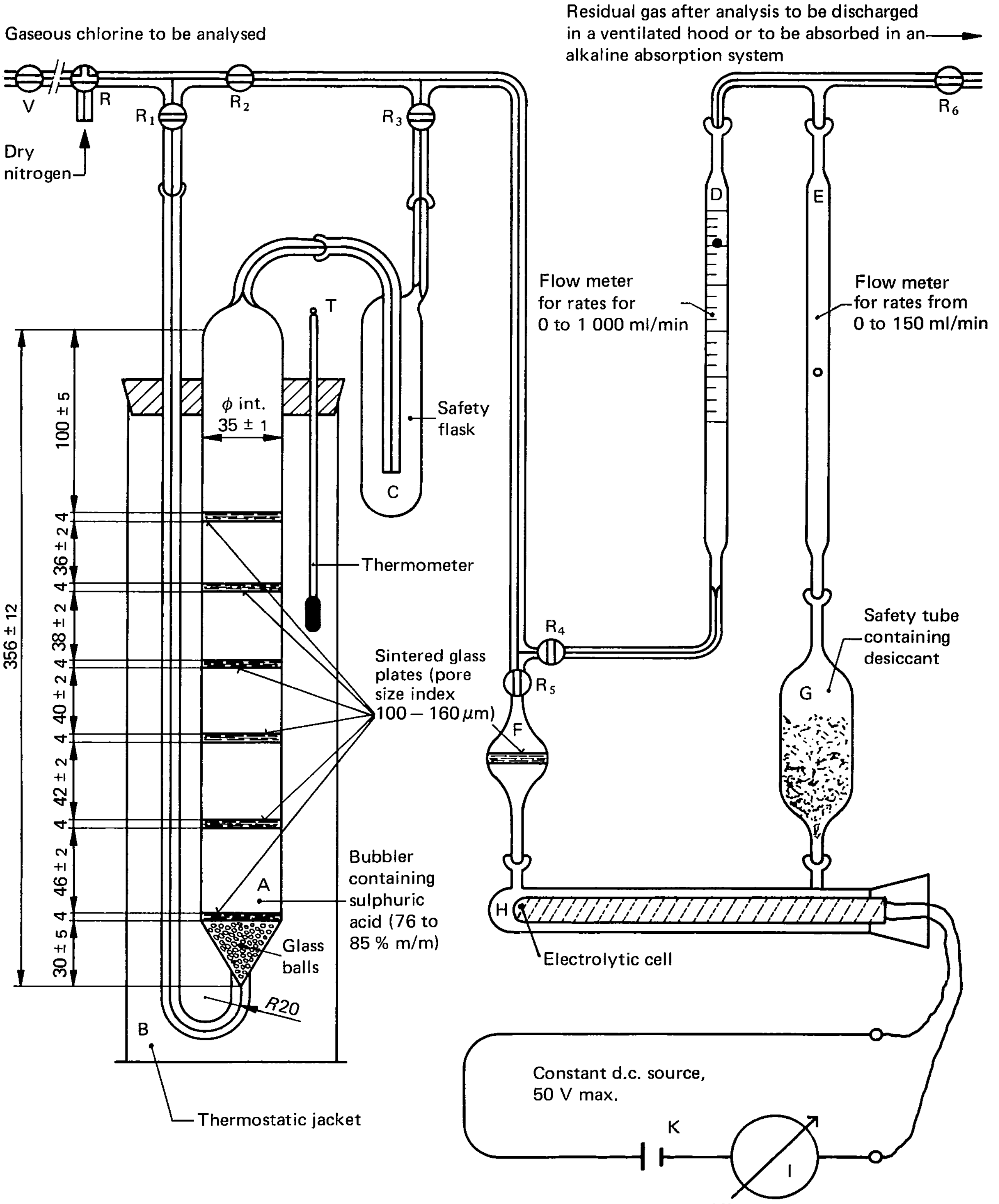

FIGURE 1 — **Diagram of electrolytic analyser**

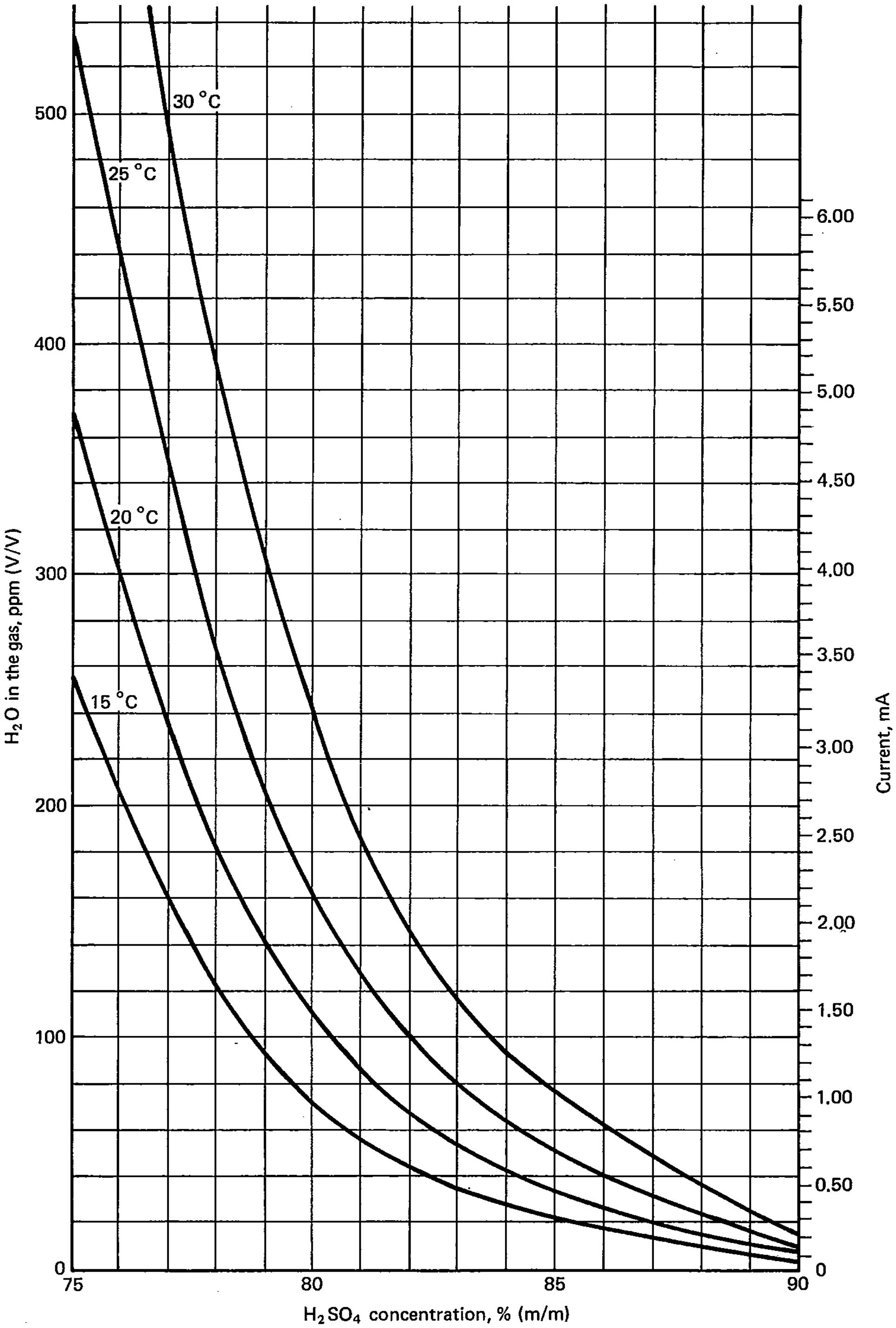

FIGURE 2 — **Equilibrium diagram showing moisture content of chlorine after bubbling in sulphuric acid as a function of acid concentration and temperature**