INTERNATIONAL STANDARD ISO 2202-1972/ADDENDUM 1

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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
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Chile
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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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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 :

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

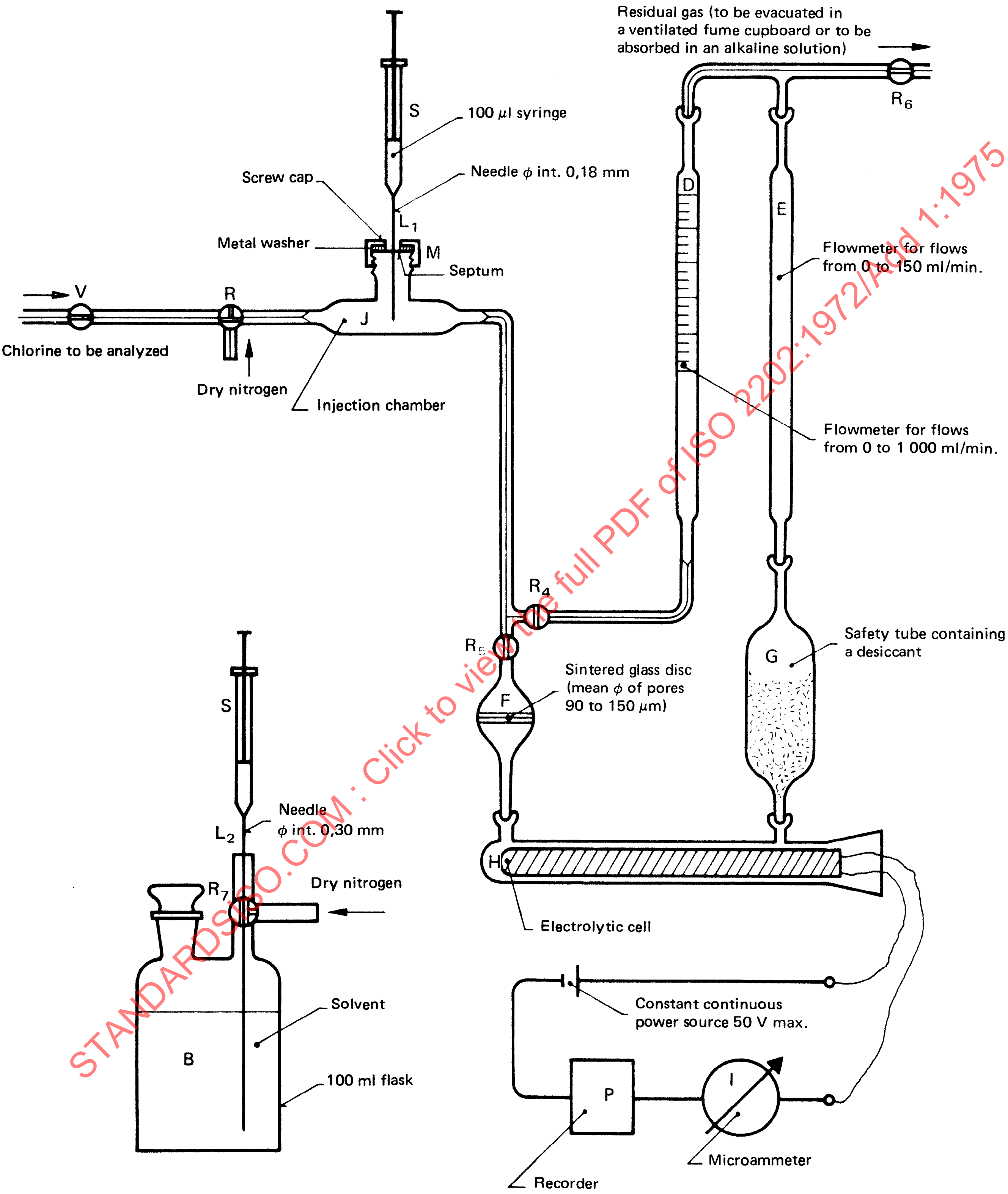

FIGURE 2 – **Device for drawing off solvent**

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

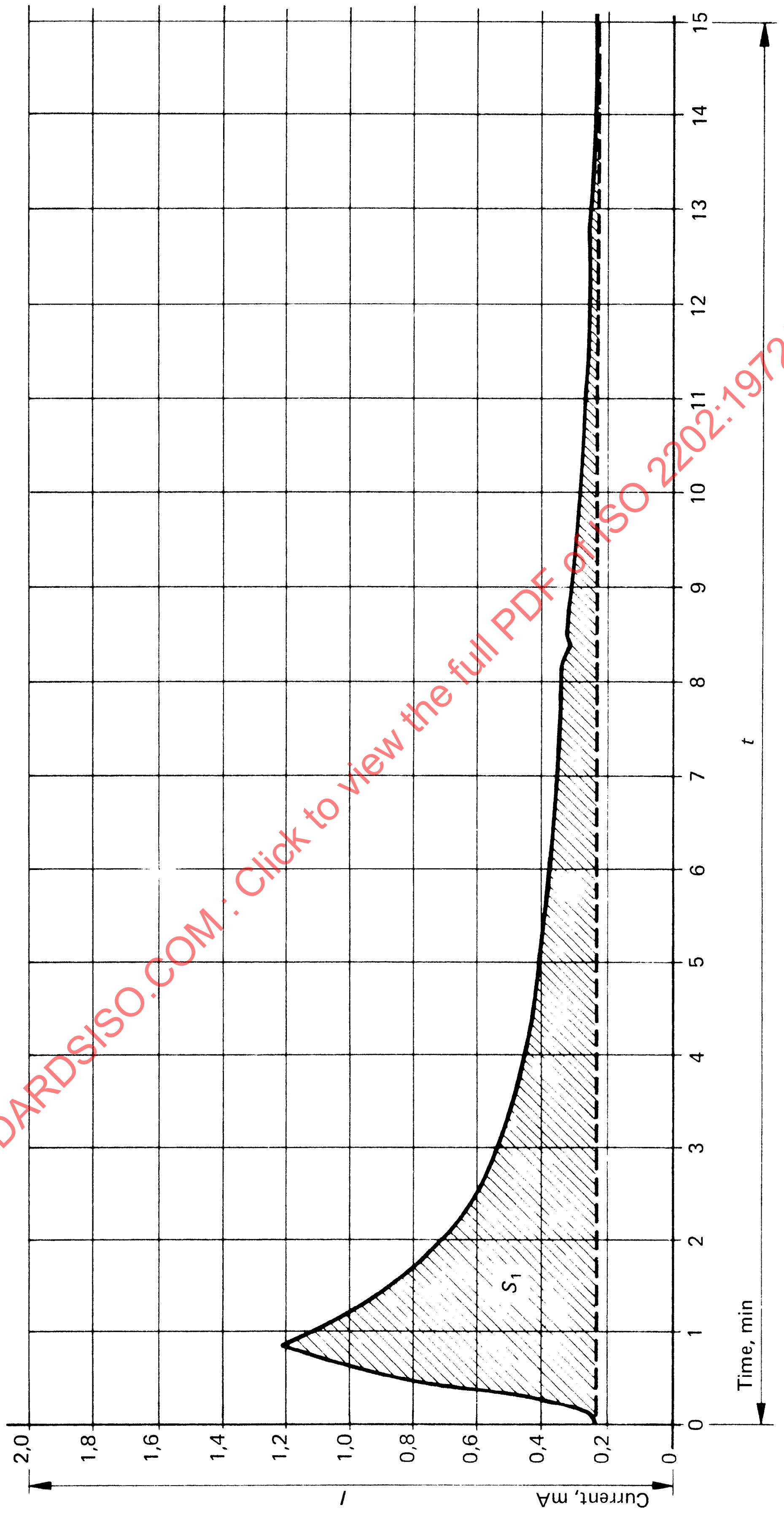

FIGURE 3 — **Typical graph**

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