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

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FOREWORD

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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

(standards.i 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 the standards at 75e76834dafc/iso-22 between 15 and 30 °C accurate to ± 0.1 °C. 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 semicapillary 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 $(R_1 \text{ to } R_6)$ 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 iTeh STANDARD 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

5.4 Safety flask (C).

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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 $100 - 160 \,\mu\text{m}$), 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 μ A, 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).

 $\mathsf{NOTE}-\mathsf{lf}$ 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 INSTRUC-TED 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 PRO-TECTIVE 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<u>ISO</u> MEANS OF A RAG SOAKED IN AMMONIA tandards.iteh.ai/catalog/star

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 2×6 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 μ A.

NOTE - During all these operations and during those described below, take care not to close ${\sf R}_6$ 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 R₁ and R₃, and close R₂ so as to pass the gas into SO 2the 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_s, and partially close stopcock R₄, passing the chlorine to be analysed into the cell (H) at a temperature of 20 \pm 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 :

96 500 coulombs correspond to 1 gram equivalent of water;

96.5 coulombs correspond to 1 milligram equivalent of water;

96.5 x 2 = 193 coulombs correspond to 1 milligram molecule of water.

Hence,

1 coulomb corresponds to electrolysis of

 $\frac{18.016}{193} = 0.0933$ mg of water, or $\frac{24.3}{193} = 0.1258$ 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 $\frac{100 \times 10^{-6}}{60}$ m³/s, a current of 1 μ A would correspond to the following water contents in the gas :

0.125 8 x
$$\frac{60}{100 \text{ x } 10^{-6}}$$
 x $10^{-6} = 0.0755 \text{ ml/m}^3$ or ppm (V/V);

PREVIEW 0.093 3 × $\frac{1}{100 \times 10^{-6}}$ × 10⁻⁶ × $\frac{1}{2.99}$ = 0.018 7 mg/kg or **PREVIEW** (m/m).

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

6.5.2.1 The water content observed on reducing the

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

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

It is convenient in practice to graduate the microammeter

Calculation of the water content, as a function of current

obtained, is carried out in accordance with the following

directly in terms of parts per million of water.

restored after 3 to 5 min.

the manufacturer's instructions.

7 EXPRESSION OF RESULTS

data :

chlorine rate to half should be half the initial value, with a: 1972 2.99 being the density of gaseous chlorine, in kilograms per maximum relative deviation of 10 % all the value read offlieds/sistCubic metre, for the conditions of analysis, that is to say at clearly greater than half, accidental entry of waters into the o-22020 °C and 760 mmHg. apparatus may be involved.

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

 1 ml/m^3 or 1 ppm (V/V) corresponds to a current of

$$\frac{1}{0.075} = 13.24 \ \mu \text{A};$$

1 mg/m³ corresponds to a current of $\frac{1}{0.0560} = 17.9 \,\mu\text{A};$

1 mg/kg or 1 ppm (m/m) corresponds to a current of

$$\frac{1}{0.018\ 7} = 53.5\ \mu A.$$

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.

3

Gaseous chlorine to be analysed

Dimensions in millimetres



Residual gas after analysis to be discharged in a ventilated hood or to be absorbed in analkaline absorption system

FIGURE 1 - Diagram of electrolytic analyser

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

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