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Rubber, raw — Determination of water content by Karl Fischer method

Caoutchouc brut — Détermination de la teneur en eau par la méthode de Karl Fischer

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 12492 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

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Introduction

The water content of raw rubber is one of the important characteristics to be determined as a quality control test. Different synthetic rubbers contain varying amounts of water. Water can affect product quality, texture, shelf life, chemical stability and reactivity. A high amount of water can cause processing difficulties.

Water contamination is a cause for major concern in a large number of applications. In the rubber industry, water is one of the major damaging contaminants and is often overlooked as a primary cause of component failure. For certain applications in the rubber industry, even a small amount of water may have damaging effects on production.

Several methods are available for the determination of water content. A Karl Fischer (KF) coulometric titrator is one of the most accurate methods. Unlike other techniques, it can trace low levels of free, emulsified and dissolved water (which cannot be detected with normal gravimetric methods). The test is capable of measuring water levels as low as 0,01 %.

Unlike gravimetric measurements, which are indirect methods that assume, all volatiles removed are water, Karl Fischer titration is a direct method that is almost specific for water. The method is especially useful for low moisture levels (<1 %).

The new test method will help to determine the water content of the raw rubber and rubber compounds in shortest possible time and will be helpful for quality control at the laboratories. Coulometric determination of water is an absolute method.

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Rubber, raw — Determination of water content by Karl Fischer method

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

CAUTION — Certain procedures specified in this International Standard may involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This International Standard specifies a test method for the determination of water content of raw rubber and compounded rubber using a coulometric Karl Fischer titration method. It applies to the water content range between 0,01 % and 1 %. As this is a very sensitive method, contact of sample with any moisture, even from the surrounding environment, must be eliminated as much as possible.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 760, *Determination of water — Karl Fischer method (General method)*

ISO 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedure*

ISO 18899:2004, *Rubber — Guide to the calibration of test equipment*

3 Principle

The water determination test (Karl Fischer method) is designed to determine the water content in substances, utilizing the quantitative reaction of water with iodine and sulfur dioxide in the presence of a lower alcohol such as methanol and an organic base, as shown in the following formulae:

$$H_2O + I_2 + SO_2 + 3\ RN \rightarrow 2(RN+H)I^- + RN{\cdot}SO_3$$

$$RN{\cdot}SO_3 + CH_3OH \rightarrow (RN+H)O\text{-}SO_2{\cdot}OCH_3.$$

There are two determination methods which differ in the way the iodine is provided: the volumetric titration method and the coulometric titration method.

In the volumetric titration method, iodine required for reaction with water is previously dissolved and the water content is determined by measuring the amount of iodine consumed as a result of reaction with water present in a sample.

In the coulometric titration method, first, iodine is produced by electrolysis of the reagent containing iodide ion, then the water content in a sample is determined by measuring the quantity of electricity which is required for the electrolysis, i.e. for the production of iodine, based on the quantitative reaction of the generated iodine with water.

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In coulometric Karl Fischer titration, iodine (I_2) is generated electrochemically from iodide (I^-). When iodine (I_2) comes in contact with the water in the sample, water is titrated according to the above mentioned reaction scheme. Once all of the water available has reacted, the reaction is complete. The amount of water in the sample is calculated by measuring the current needed for the electrochemical generation of iodine (I_2) from iodide (I^-) according to the following reaction:

$$2I^- \rightarrow I_2 + 2e^-$$

According to Faraday's Law, the quantity of the iodine produced is proportional to the current generated. In the above equation, I_2 and H_2O react with each other in proportion of 1:1. Therefore, a mole of water (18 g) is equivalent to 2 × 96 500 coulombs, or 10,72 coulombs/1 mg of H_2O.

Conveying the water contained within the sample to the titration cell is an important part of the titration. The volumetric flow rate of the carrier (nitrogen) gas is precisely controlled by the flow controller. The sample remains in the sample boat. The carrier gas is dried by passing it through silica gel and zeolite type desiccants. The dry carrier gas enters the sample heating chamber and carries the total moisture into the titration cell. The carrier gas passes through the titration cell as long for as the sample is being heated. In this process, the major quantity of water is released at the beginning. The set-up and the connection of the oven are illustrated by the figure below:

N_2 ⟶ Drying ⟶ Oven ⟶ Titration Cell

Thus, the total amount of moisture can be determined by measuring the total consumption of electricity.

4 Reagents

4.1 Water standard for coulometric Karl Fischer titration, 0,1 % (NIST Traceable).

4.2 Anode solution (for use when a titration cell with a diaphragm is being used).

4.3 Cathode solution (for use when a titration cell with a diaphragm is being used).

4.4 Universal reagent (for use when a titration cell without a diaphragm is being used).

4.5 Dry N_2 gas of instrument grade.

4.6 Aluminium oxide.

4.7 Ethanol.

4.8 Concentrated HNO_3.

4.9 Hexane.

5 Apparatus

5.1 Coulometric Karl Fischer titrator with evaporator. Different components of coulometric Karl Fischer titrator are shown in Figure 1.

The water evaporator consists of an oven capable of heating the test portion to 300 °C, a heating tube, a temperature control unit, a carrier-gas flow meter and carrier-gas drying tubes containing desiccant.

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5.2 Analytical balance, capable of weighing to the nearest 0,0000 1 g.

5.3 Micro-syringe, calibrated.

5.4 Sample holder.

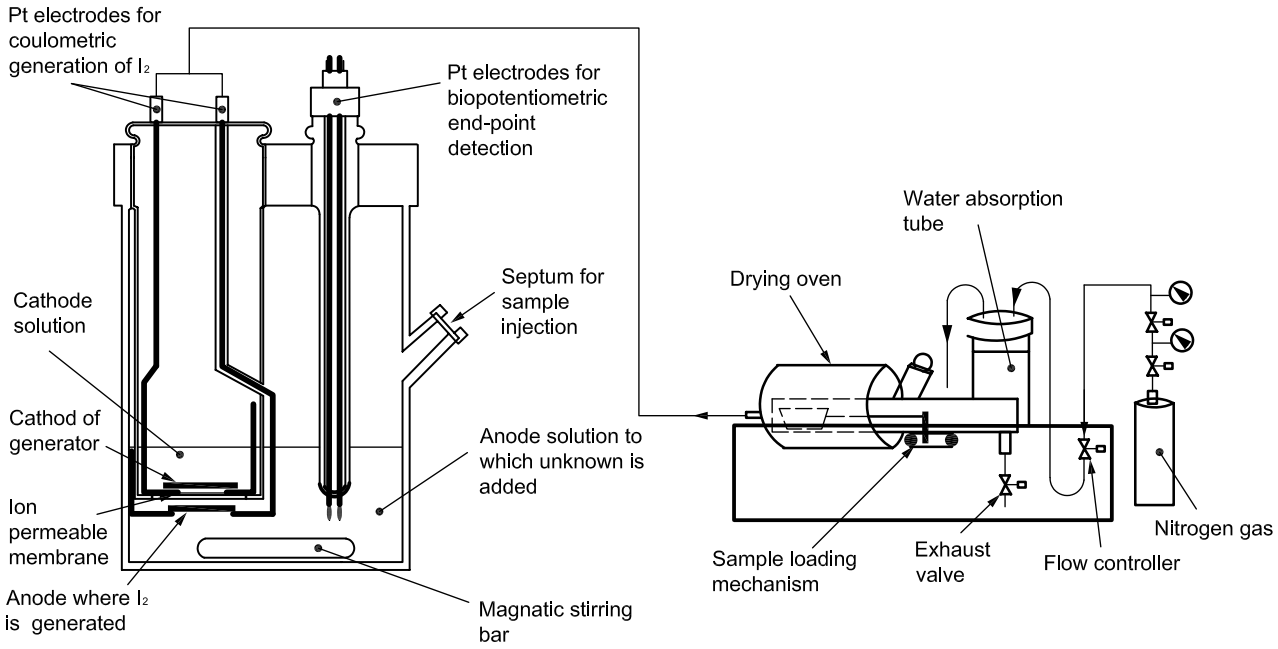

Figure 1 — Different components of coulometric Karl Fischer titration equipment

6 Calibration

6.1 Standardize the instrument using a traceable water standard (4.1) and determine the % water content to check the recovery.

6.2 The test apparatus shall be calibrated in accordance with the schedule given in Annex A.

7 Sampling and preparation of test piece

7.1 Take the laboratory sample in accordance with the method specified in ISO 1795 and prepare the test piece of 0,5 g to 1 g from the laboratory sample. Cut the test piece into small thin pieces using suitable tools such as scissors or a knife.

7.2 The test piece size should be small so that as many tests as possible can be carried out using the same electrolyte solution and the titration time can be kept short.

8 Procedure

8.1 Power on

Turn on the power to the instrument as per the instructions of the instrument manufacturer.

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8.2 Selection of the generator electrode

The generator electrode without diaphragm is the best choice for most applications. However, the generator electrode with diaphragm shall be used when samples contain ketone and aldehyde groups, because special reagents for aldehyde and ketone are only available for generator electrodes with diaphragms. If a low conductivity solvent like chloroform is used because of the solubility of the sample, then a generator electrode with a diaphragm is the first choice. Ensure safety precautions as per the equipment manual.

8.3 Filling the electrolysis cell

8.3.1 Generator electrode without diaphragm

Fill the cell with universal reagent (4.4) according to the instructions of the instrument manufacturer.

8.3.2 Generator electrode with diaphragm

Fill the anode chamber and the cathode chamber with anode solution (4.2) and cathode solution (4.3) according to the instructions of the instrument manufacturer.

8.4 Equipment check

8.4.1 Reagent change

In the following cases, the electrolyte solutions should be changed:

a) when the capacity of the reagent is exhausted;

b) if the drift is too high;

c) if during analysis the error message appears.

8.4.2 Indicator electrode

Clean the electrode according to the instruction of the instrument manufacturer.

8.4.3 Cleaning

8.4.3.1 Generator electrode with diaphragm

a) Sometimes resinous material is deposited on the diaphragm. Hang the generator electrode vertically from a support rod, fill with concentrated HNO_3 (4.8) and allow to stand overnight. Rinse the electrode with water and then with ethanol (4.7).

b) If there is a deposition of oil on the electrode, wash the electrode with hexane (4.9) and then rinse with ethanol.

c) To clean the diaphragm, fill the cathode compartment of the generator electrode with methanol and allow it to drain out. Repeat this process two to three times.

8.4.3.2 Generator electrode without diaphragm

If there is a deposition of oil on the electrode, wash the electrode with hexane (4.9) and then rinse it with ethanol (4.7).

Dry all parts thoroughly after cleaning. A hot-air blower can be used to dry the parts. If the parts are dried in an oven, care should be taken to ensure that the temperature does not exceed 70 °C.

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8.4.4 Checking the instrument

8.4.4.1 The instrument can be checked with traceable water standard solutions with a water content of 1,00 mg/g ± 0,05 mg/g and/or 0,10 mg/g ± 0,01 mg/g. This is being done to check whether the instrument is working properly or not.

8.4.4.2 When the instrument is stabilized and ready to operate, press the start switch and carefully inject a measured amount of the water standard (4.1) into the titration chamber using the calibrated micro-syringe (5.3). Record the reading when the analysis is completed. Generally, 1 g of water standard of water content of 1,00 mg/g ± 0,05 mg/g will give 1 mg of water.

8.5 Analysis

8.5.1 Stabilize the instrument for at least 30 min. During the stabilization period, the evaporator and reaction vessel of the instrument should be purged with dry nitrogen (water free) (4.5). The evaporator should be kept at high temperature during the stabilization period.

8.5.2 The evaporation oven temperature shall be adjusted as indicated in Table 1, depending on the type of rubbers.

Table 1 — Stabilization temperature for different rubber

Name of rubber	**Stabilization temperature** °C
Natural Rubber (NR), Styrene Butadiene Rubber (SBR), Polybutadiene Rubber(BR)	120
Thermoplastic Rubbers	150
Acrylic Rubbers and Silicone Rubbers	160

8.5.3 Select the test piece size based on the water content as shown in Table 2.

Table 2 — Test piece mass against water to be determined

Water content % by mass	**Mass of the test piece** g
1 %	0,01 to 0,1
0,1 %	0,1 to 1
0,01 %	1

8.5.4 Take the test piece as per Table 2 to the nearest milligram. Immediately, place the test piece in the sample tube.

8.5.5 Purge the sample compartment of the evaporator continuously to avoid any water deposition.

8.5.6 Put the sample in the sample tube according to the instructions of the instrument manufacturer.

8.5.7 Press the “START” button of the instrument, stop the purge gas supply and allow the carrier gas to circulate.

NOTE The water quantity absorbed in the solvent is titrated within a short period of time. If the drift is not reached, or almost not reached, this is indicative of a side reaction.

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8.5.8 Allow the titration until the display shows the results in %, ppm or µg.

8.5.9 Note the reading of the water content.

8.5.10 Use following equation for estimating water content, *M*, in percentage.

$$M = \frac{m_{MO}}{m_{TP}} \times 10^{-4}$$

where

m_{MO} is the mass of water found in the test piece, expressed in micrograms;

m_{TP} is the mass of the test piece, expressed in grams.

The effect of drift (background) and/or other factors may be compensated automatically by the instrument or manually.

9 Precision

Precision of the test method is to be determined.

10 Test report

The test report shall include the following information:

a) sample details:
   1) full description of the sample and its origin;
   2) method of preparation of test piece from the sample;

b) test method:
   1) a full reference to the test method used, i.e. the number of this International Standard;
   2) the test procedure used;
   3) the type of test piece used:

c) test details:
   1) the laboratory temperature;
   2) the time and temperature of conditioning prior to test;
   3) the temperature of test, if other than standard laboratory temperature and the relative humidity if necessary;
   4) details of any procedures not specified in this International Standard;

d) test results:
   1) the number of test pieces used;
   2) the individual test results;
   3) the mean results;

e) date(s) of test.

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Annex A
(normative)

Calibration schedule

A.1 Inspection

Before any calibration is undertaken, the condition of the items to be calibrated shall be ascertained by inspection and recorded on any calibration report or certificate. It shall be reported whether calibration is made in the 'as-received' condition or after rectification of any abnormality or fault.

It shall be ascertained that the apparatus is generally fit for the intended purpose, including any parameters specified as approximate and for which the apparatus does not therefore need to be formally calibrated. If such parameters are liable to change, then the need for periodic checks shall be written into the detailed calibration procedures.

A.2 Schedule

Verification/calibration of the test apparatus is a normative part of this International Standard. The frequency of calibration and the procedures used are, unless otherwise stated, at the discretion of the individual laboratory using ISO 18899 for guidance.

The calibration schedule given in Table A.1 has been compiled by listing all of the parameters specified in the test method, together with the specified requirement. A parameter and requirement can relate to the main test apparatus, part of that apparatus or to an ancillary apparatus necessary for the test.

For each parameter, a calibration procedure is indicated by reference to ISO 18899, to another publication or to a procedure particular to the test method which is detailed (whenever a more specific or detailed calibration procedure than in ISO 18899 is available, it shall be used in preference).

The verification frequency for each parameter is given by a code-letter.

The code letters used in the calibration schedule are

— R Use of certified reference material

— U In use

Table A.1 — Calibration frequency schedule

Parameter	Requirement	Sub clause in ISO 18899:2004	Verification frequency guide	Notes
Temperature	Accurate to ± 1°C	18	U	Calibrated thermometer
Weight	Accurate to ± 0,01 mg	22.2	R	Calibrated weight
Reference materials	Thermometer, Reference weight			
Reagent	Standard water solution for cell verification			

In addition to the items listed in the table, use of the following is implied, which needs to be calibrated in accordance with ISO 18899:

— a thermometer for monitoring the conditioning and test temperatures.

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