

Technical bulletins for testing packaging systems

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Testing plastic materials – optical method for determination of the oxygen permeability of packaging systems (films and molded components)



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1 Area of application

This test protocol describes a method for determining the oxygen permeability of packaging materials. It applies for the temperature range from 0°C to 60°C. It is assumed that the packaging materials are used in this temperature range.

The test method is suitable for determining the oxygen permeability of flat packaging materials and molded parts. It can be used for the following oxygen permeability ranges:

- Flat packaging materials: 10^{-2} to 10^6 cm³ (STP)/(m²·d·bar)
- Molded parts: 10^{-4} to 10^4 cm³ (STP)/(packaging·d·bar)

(STP = standard temperature and pressure. Standard temperature = 273.15K = 0°C. Standard pressure = 101.325 Pa = 1.01325 bar = 760 Torr = 1 atm)

2 References to other standards

This test standard contains specifications from other publications, indicated by dated or undated references. These references are cited at the relevant positions in the text, and details of the publications are given below. For dated references, subsequent amendments or changes to these publications only apply to this standard if they are incorporated by amendment or change to the standard. For undated references, the most recent version of the publication applies.

DIN 53380 Part 3: Testing plastic materials: Determination of the gas permeability; Part 3: Oxygen-specific carrier gas method for measurements on plastic films and molded plastic parts

DIN 50008-1: Climates and their technical application – constant climates above aqueous solutions – saturated salt solutions, glycerol solutions

DIN 53370: Testing plastic films – measurement of thickness via mechanical scanning

3 Definitions

The following definitions apply when using this standard (DIN 53380 Part 3):

3.1 *Area-related oxygen permeability*

For flat test specimens of constant thickness (e.g. films), the area-related oxygen permeability is the volume of oxygen referring to the standard state 2) that permeates the test specimen per unit area, time, and oxygen partial pressure.

3.2 Oxygen permeability for hollow specimens

For hollow specimens, whose surface cannot be accurately measured and/or whose wall thickness is not constant, the hollow specimen related oxygen permeability is the volume of oxygen in the standard state that permeates the test specimen per unit time, and oxygen partial pressure.

4 Brief description of the test method

4.1 Measurements on films

The films are mounted between the two parts of the test chamber [Figure 3]. One part of the test chamber is flushed with nitrogen, the other with oxygen. The oxygen permeating through the film into the part of the chamber that was flushed with nitrogen is detected via an optical sensor. This sensor is in the part of the chamber that was flushed with nitrogen.

4.2 Measurements on hollow specimens

The hollow specimens are flushed with nitrogen and then sealed. The oxygen acts on the hollow specimen from the outside.

5 Materials used for the tests

5.1 Carrier gas

The carrier gas is nitrogen. It must be dry. The amount of oxygen in the nitrogen must not exceed 0.01% by volume.

5.2 Oxygen and oxygen mixtures

The oxygen gas must be dry and must contain at least 99.5% by volume oxygen. If oxygen mixtures are used (preferably oxygen with nitrogen), then the volume oxygen content must be known to an accuracy of at least $\pm 0.5\%$ by volume.

5.3 Vacuum grease

Vacuum grease is used to seal the test specimen on the smooth surface of the upper part of the test chamber and on the sealing ring of the lower part of the test chamber.

5.4 Adhesives

The bonded joints that are necessary when testing hollow specimens must be made with a 2-component adhesive. Rapid-curing adhesives based on methyl methacrylate or epoxy resin have proven successful for this.

6 Description of components of the test equipment

6.1 Gas connections

All the connections in the metal gas lines must be gas-tight (oxygen permeability $< 10^{-4} \text{ cm}^3 \text{ (STP)/day}$). Cutting ring couplings have proven very successful for this.

6.2 Gas humidification

Various methods can be used for defined humidification of gases. Two commonly used methods for setting the humidity, which are easy to technically realize, are recommended (DIN 53380 Part 3):

6.2.1 Saturated salt solutions

The gases are passed through saturated salt solutions. Suitable salt solutions are described in DIN 50008-1. These give constant climates of, for example, 12, 33, 53, 75, 85, and 93% relative humidity at 23°C. The gas wash bottles having a volume of about 250 cm³ are approximately 1/3 filled with the salt solution (including the solid salt). The surface area of the salt solution should be at least 15 cm². The gas inlet into the gas wash bottle is below the surface of the salt solution but above the solid salt. This allows visual monitoring of the gas flow via the gas bubbles.

6.2.2 Saturated vapor pressure

The gas to be humidified is passed through distilled water having a specific temperature. At a temperature of 23°C this allows the relative humidity of the gases to be adjusted in the range from 22% to 100%. The gas wash bottle must be held at the saturation temperature by means of a thermostat, in order to achieve the desired relative humidity from tables of the water vapor pressure.

6.2.3 Valves

Using 4 two-way valves the gas streams (nitrogen/oxygen) to the test chambers can be switched on and off.

6.2.4 Sensors

The sensor system consists of a sensor spot with a fluorescent oxygen-sensitive film, an excitation source (LED), an optical fiber, and a detector system (photodiode) that can measure fluorescence. There is an optical filter in front of the photodiode that only allows passage of the emitted red light and prevents extraneous light (e.g. excitation light) hitting the photodiode. Figure 1 shows a schematic representation of the optical system.

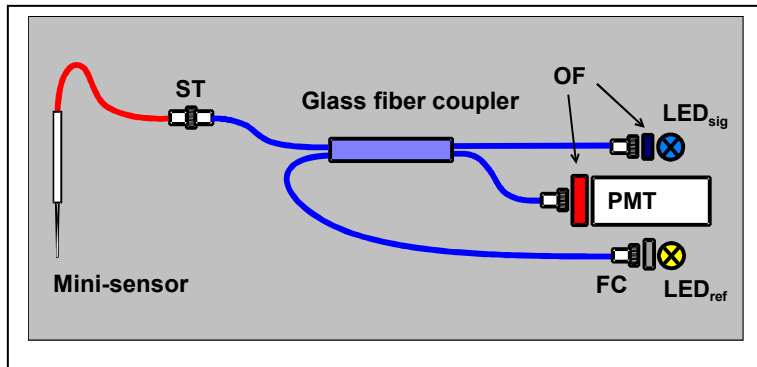


Figure 1: Schematic representation of the optical measurement system with mini-sensors. (LED: Light Emitting Diode, PD: Photodiode, OF: Optical Filter, FC: Fiber Connection)

The principle of the optical-chemical oxygen measurement is based on the quenching of the luminescence by molecular oxygen. This principle is shown in Figure 2.

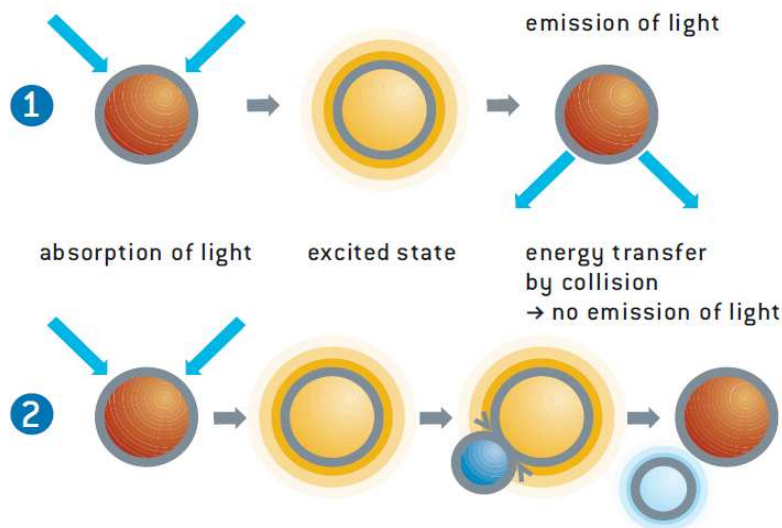


Figure 2: Principle of dynamic quenching of luminescence by molecular oxygen
 (1) Luminescence process without oxygen
 (2) Deactivation of the luminescent indicator molecule by molecular oxygen

The oxygen sensors contain an indicator pigment (luminophore). Blue-green light (wavelength: 505 nm) causes this to convert into an excited state. In the absence of oxygen the excited luminophore emits the absorbed energy as red light (1).

In the presence of oxygen there is quenching of the luminescence due to collision of the excited luminophore with the quencher (oxygen). This results in deactivation of the luminophore without the emission of radiation (2). On collision there is energy transfer from the excited indicator molecule to the oxygen, and the latter converts from the ground state (triplet state) to the excited singlet state. As a

result, the luminescence signal of the indicator molecule decreases. The oxygen concentration hence correlates with the duration of the luminescence and can thus be measured via the emitted red light.

The indicator pigment is embedded in a polymer matrix that is permeable to oxygen molecules. This is a very hydrophobic matrix which prevents interfering ions and pH changes causing cross-sensitivities. The oxygen-sensitive layer is applied as an indicator/matrix cocktail to the end of an optical fiber or as a thin film (thickness ca. 200 μm) to a support material. The oxygen molecules diffuse through the sensor membrane to the indicator pigment. They quench the optical emission (fluorescence) of the indicator pigment. The fluorescence of the indicator pigment decreases in proportion to the number of oxygen molecules that are present.

The system measures the luminescence decay time, which is also termed the lifetime. The phase modulation technique is used to determine this. In this technique the fluorescence of the indicator pigment is excited by sinusoidally modulated light. The resulting sinusoidal fluorescent light has the same frequency as the excitation light but is shifted in time by phase Φ . This phase shift can be used to determine the fluorescence decay time τ . The latter is a function of the oxygen concentration.

Measurement of the decay time is preferred to measurement of the intensity for the following reasons:

- Unlike the intensity, the decay time is independent of fluctuations in the intensity of the light source and in the sensitivity of the sensor.
- Signal loss due to the bending of the fiber or intensity changes due to changing the sensor geometry have no effect on the measurement result.
- Above a certain minimum signal strength, the measurement signal is independent of the indicator concentration. (Photo-bleaching and leaching out of the indicator pigment hence have no effect on the decay time and hence the measurement result. With measurement systems based on intensity measurement, photo-bleaching and leaching out of the indicator pigment lead to decrease of the measurement signal and hence to erroneous results.)
- The decay time is independent of changes in the optical properties, including the refractive index and coloration.

Advantages over other oxygen sensors:

- In contrast to conventional amperometric sensors, the optical sensors do not consume their analytes in the measurement process.
- Although the so-called "stirring effect" occurs in electrodes, the measurement signal is independent of the flow rate and stirrer speed.
- The optical measurement signal can be transmitted virtually loss-free over large distances and is not affected by electromagnetic fields.
- The optical decay sensor is suitable for use in both liquid and gaseous media, unlike a flow cell or the impulse method.

NOTE: Other sensors can also be used provided they possess the following properties:

- Measuring range in gas: 0 to 4000 Pa oxygen

- Measurement limit: 2 Pa oxygen
- Measurement resolution: 1 Pa oxygen
- Insensitivity to moisture
- No reaction with oxygen

6.2.5 Data recording

Manual recording after reading the digital indicator or data acquisition by computer.

7 Calibration of the sensor

The sensor can be calibrated by measuring the oxygen concentration of a calibration gas ($p_{O_2}=1000$ or 2000 Pa) or by measuring the permeation through a calibration film (e.g. $100\ \mu\text{m}$ PET film).

8 Preparation and shape of the test specimens

8.1 Flat packaging materials

Test specimens are taken from various positions distributed over the surface. These specimens must be representative and must not have defects (e.g. undesired holes) or any visible damage (e.g. creased sections). If a permeation coefficient has to be calculated, the thickness of the specimens must be measured with a thickness gauge in accordance with DIN 53370. If the test specimens are composed of several layers securely attached to each other (laminate), the sides must be marked and in the test report the side penetrated by the oxygen and the relative humidity must be indicated.

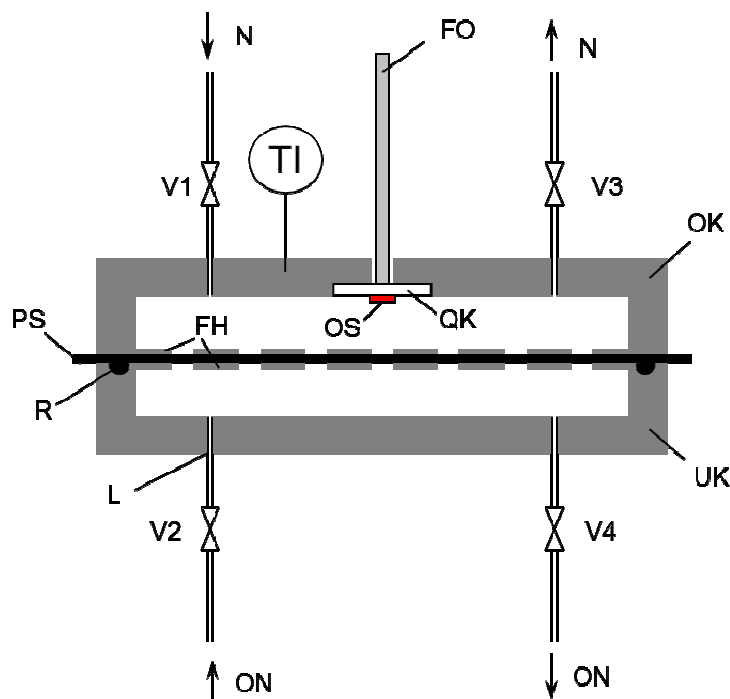
8.2 Hollow objects

The hollow objects, and in particular hollow containers with contents, must be representative of the product. In many cases it is necessary to empty the container prior to the test. This must be undertaken as carefully as possible. The opening that is cut in the container for this purpose must only be as large as necessary. This opening must be made in such a way that it can subsequently be easily resealed gas-tight using a two-component adhesive.

9 Testing flat packaging materials

9.1 Test chamber for flat packaging materials

The test chamber (see Figure 3) in which the test film is mounted consists of 2 metal parts of circular cross-section. After mounting the film the free film surface for measurement is between 50 and 200 cm². The total volume of the two chambers must be between 20 and 200 cm³. The temperature of the upper half of the chamber is measured using a thermometer. The lower half of the chamber is sealed against the mounted film with an O-Ring such that it presses the film against the flat edge of the lower half of the chamber, as close as possible to its inner edge. The lower part of the chamber (sensor side) has a flat edge of 5 to 10 mm width. As this edge is the critical sealing zone, against which the film is pressed, it must be smooth and undamaged. The inner diameter of the lower half of the chamber determines the area of permeation of the film. For controlling the temperature of the test cell in the range from 0°C to 60°C, the test chambers must be placed in a hot-cold test cabinet. Another possibility is to use chambers whose temperature can be set using a liquid thermostat.



OS	Optical O2 sensor
QK	Quartz glass
FO	Optical fiber
PS	Packaging material
FH	Film holder
R	O-ring
L	Inserted metal tube (gas-tight)
OK	Upper test chamber
UK	Lower test chamber
ON	O2 or N2 line
N	N2 line

Figure 3: Schematic representation of the test chamber for testing films

9.2 Test procedure

The test involves two procedural steps. (1) After inserting the test specimen, the measurement system is first of all checked for tightness. To do this both sides of the test specimen are flushed with nitrogen. The valves are then closed. The oxygen increase in the upper test chamber is then recorded as the baseline (= zero value).

(2) The side of the test specimen without the oxygen sensor is then flushed with oxygen. The stationary increase in oxygen in the upper test chamber minus the zero value gives the permeability of the test specimen.

Figure 4 shows measurement data for the example of a 100 μm PET film. Two regions can clearly be seen: the zero value measurement region and the actual permeation measurement using oxygen as the test gas.

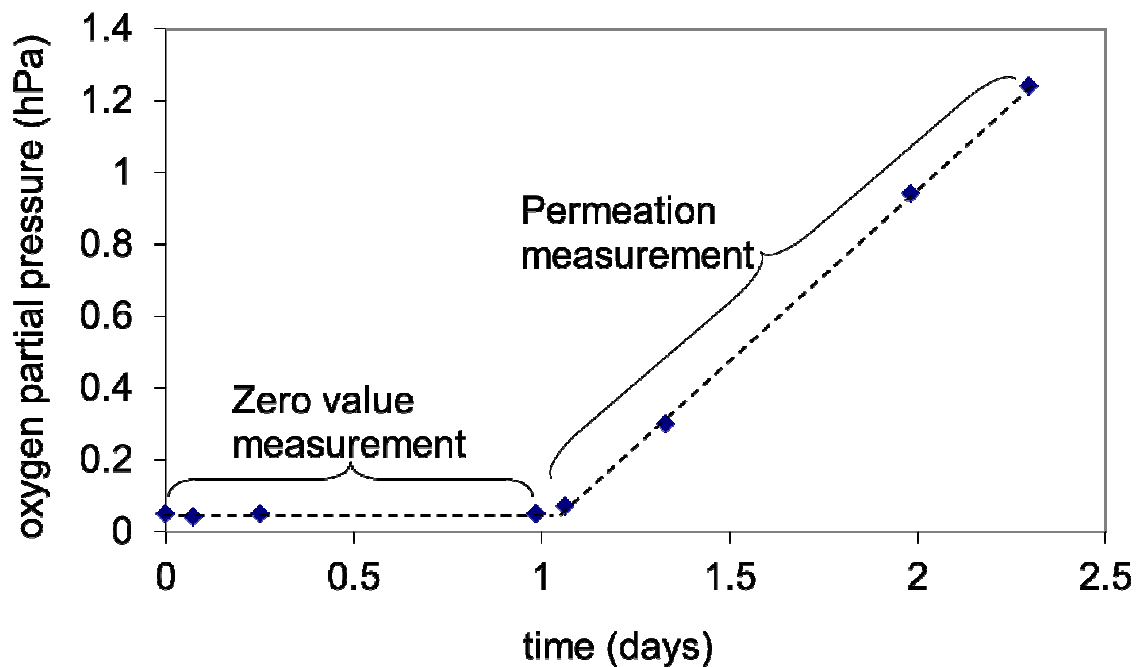


Figure 4: Oxygen permeability measurement data for the example of a 100 μm PET film

Insertion of the test specimen and flushing: After opening the test chamber a thin layer of vacuum grease is applied to the sealing surface on the upper half of the test chamber. To prevent deformation of the packaging due to gravity or pressure differences (between the upper and lower halves of the test chamber), grid-holders are inserted above and below the test specimen. They stop the specimen sagging or deforming during the measurements, which would change the gas volume in the two halves and so distort the results. In order to prevent the permeation surface decreasing due to the presence of the grid-holder, tissue paper is inserted between the film and the two holders. There must be no tissue paper on the sealing surface. The gas volume in the upper half of the test chamber influences the increase in oxygen partial pressure in the upper test chamber. Accordingly, the test specimen is

laid on the lower half of the test chamber that is fitted with a sealing ring and then carefully smoothed. The upper part of the test chamber is now placed on the lower part and depending on the design is either screwed down or clamped in position. The test chamber is now sealed and gas-tight. Carrier gas is now let into the two halves of the test chamber by means of valves V1 and V2 at a flow rate of 500 to 1000 cm³/min in order to remove the air. Valves 1 to 4 are closed again after 5 minutes.

9.3 Determination of the zero value

The zero value must be determined before the start of the actual measurements. To do this the two halves of the test chamber are filled with nitrogen as described in section 9.2 and the increase in the oxygen concentration over time is then measured. The increase in the oxygen concentration (namely the zero value) is caused by the outgasing of the test specimen, or a non-tight system, or a combination of these two effects.

The zero value must if possible not exceed 0.2 cm³/(m²·d·bar). If the value is higher than this then the cause must be found and alleviated. The zero value for highly permeable packaging materials (oxygen permeability >1000 cm³/(m²·d·bar)) may be significantly higher than 0.2 cm³/(m²·d·bar). In this case the zero value can be neglected.

9.4 Determination of the oxygen permeability

As soon as the zero value has been determined, oxygen is passed into the lower half of the test chamber via valve V2 (see Figure 3) at a flow rate of 500 to 1000 cm³/min. The flushing time is about 5 minutes. The oxygen concentration in the upper half of the test chamber, which is indicated by the optical sensor, increases after a certain breakthrough time and then increases linearly with time. The breakthrough time depends on the type of plastic and its thickness and can vary from seconds (e.g. for thin polyolefin films) to days (for advanced high-barrier films).

Note: In the described test method the difference in partial pressure between the two sides of the film is assumed to be quasi constant during the measurements. For measurements over a very long period the graph of the oxygen concentration against time is exponential. For exponential functions the initial region can be assumed to be linear.

10 Testing hollow objects

The optical sensor can also be used to measure permeation through hollow objects. A distinction must be made between closed and open hollow objects (see DIN 53380-3).

10.1 Closed hollow objects

Closed hollow objects (packaging units) are deemed to be packaging systems in which the contents is sealed gas-tight on all sides from the outside atmosphere. In general the contents must be removed from the packaging prior to testing. Utmost care must be taken so that the emptying of the packaging

does not cause any damage which could give rise to erroneous results in the subsequent permeation test. The opening to remove the contents must generally be made at a smooth, easily accessible position on the packaging. As the effectiveness of the seal/seam is of special interest when testing packaging, it is vital that the original seal/seam remains untouched. After emptying the packaging, the opening is resealed with a pore-free, gas-tight adhesive (see section 5.4) (Figure 5).

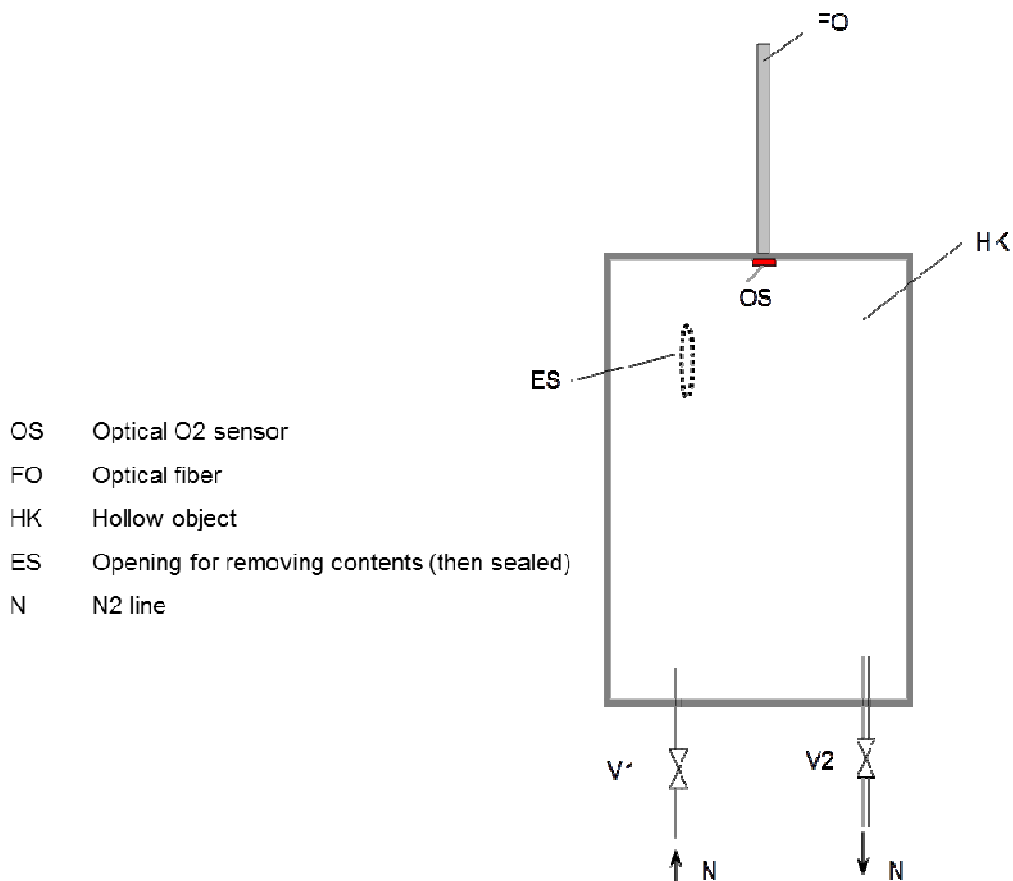


Figure 5: Schematic representation of a system for measuring the oxygen permeability of closed hollow objects

The tests on hollow objects can be measured using air (20.9 volume % oxygen) or using an enclosure in the form of a rigid glass or metal bell placed on the flat lower part of the equipment, as described for example in DIN 53380 Part 3.

10.2 Open hollow objects

Open hollow objects are all objects which contain at least one opening. These include plastic bottles and deep-drawn plastic trays for packaging purposes, not yet sealed with a lid. Prior to testing, the openings on these objects are sealed gas-tight by bonding suitable pieces of a thick aluminum foil onto them using a two-component adhesive. After curing the adhesive the objects are tested in the same way as closed objects (see section 10.1). Another option is to bond open, hollow dish-like or beaker-like objects to a base plate (see Figure 6).

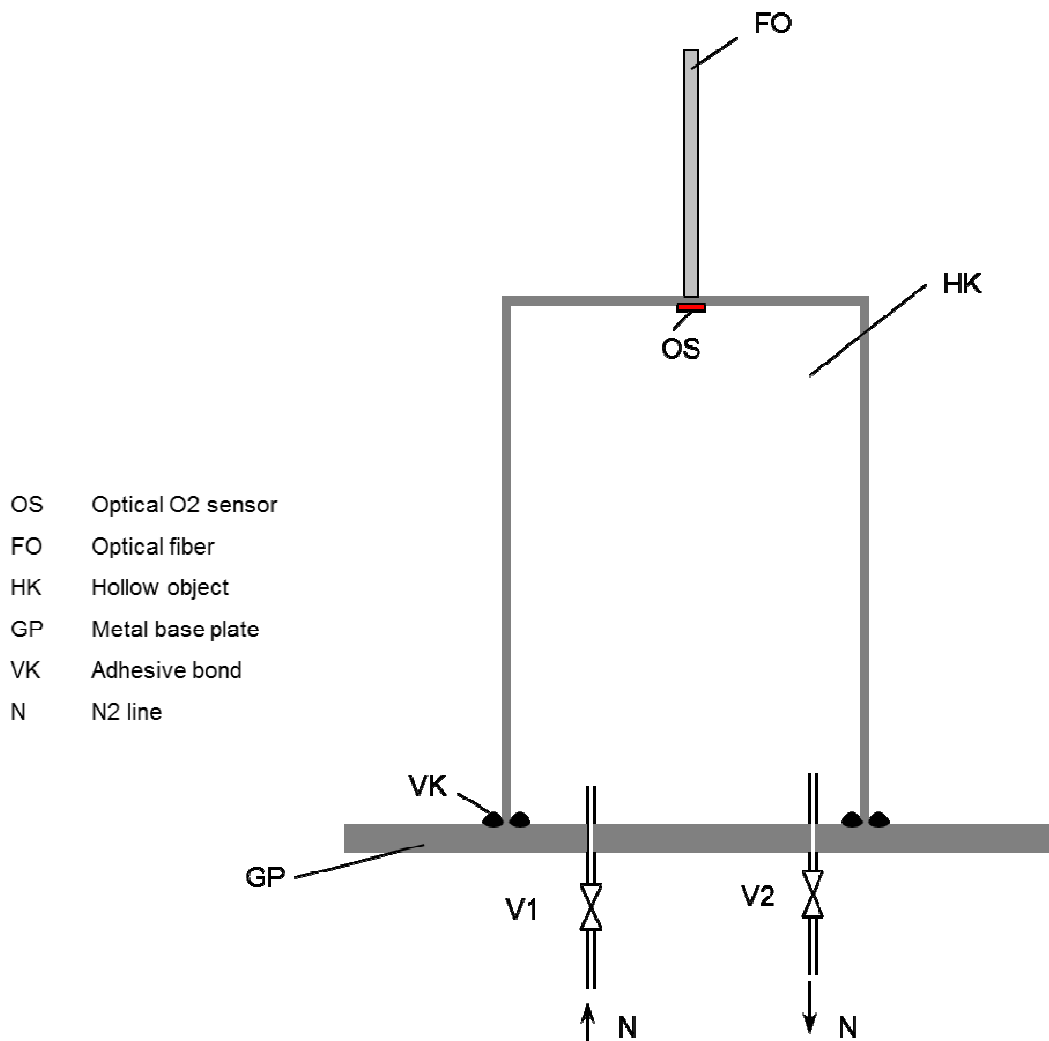


Figure 6: Schematic representation of a system for measuring the oxygen permeability of open hollow objects

The tests on open, hollow objects can also be measured using air (20.9 volume % oxygen) or using an enclosure in the form of a rigid glass or metal bell placed on the flat lower part of the equipment, as described for example in DIN 53380 Part 3.

11 Evaluation

The oxygen permeability is calculated using the following equations:

11.1 Area-related oxygen permeability

According to the ideal gas law:

$$\dot{p}_{O_2} \cdot V_{test\ cell} = p_{std} \cdot \dot{V}_{O_2}(STP) = \dot{n}_{O_2} \cdot R \cdot T_{std}$$

If the measurement is carried out at 296K (= 23°C), instead of the standard temperature 273K (= 0°C), the permeability Q can be calculated using the following equation:

Equations:

$$Q = \frac{\dot{p}_{O_2} \cdot V_{test\ cell}}{p_{std} \cdot A \cdot \Delta p_{O_2}} \cdot \frac{T_{std}}{T_{meas}}$$

Symbol	Explanation	Units
\dot{p}_{O_2}	Increase in oxygen partial pressure in the upper test chamber (UTC)	hPa · d ⁻¹
$V_{test\ cell}$	Volume of the UTC	cm ³
p_{std}	Standard pressure	1013 hPa
$\dot{V}_{O_2}(STP)$	Oxygen volume flow into the UTC under standard conditions	cm ³ (STP) · d ⁻¹
\dot{n}_{O_2}	Molar mass flow into the UTC	mol · d ⁻¹
R	Gas constant	8.314 J · mol ⁻¹ · K ⁻¹
T_{std}	Standard temperature	273K
T_{meas}	Measurement temperature	K
Q	Permeability	cm ³ · m ⁻² · d ⁻¹ · bar ⁻¹
Δp_{O_2}	Difference in oxygen partial pressure between the lower and upper test chamber	bar

The difference in oxygen partial pressure Δp_{O_2} is the difference between the oxygen partial pressure in the lower and upper halves of the test chamber. The lower half of the test chamber is completely filled with oxygen (100 volume %). Hence the oxygen partial pressure here equals the atmospheric pressure.

11.2 Packaging-specific oxygen permeability

Analogous to the area-specific oxygen permeability, the following equation can be used for calculating packaging-specific oxygen permeability:

$$Q = \frac{\dot{p}_{O_2} \cdot V_{packaging}}{p_{std} \cdot \Delta p_{O_2}} \cdot \frac{T_{std}}{T_{meas}}$$

There is no area term here, and instead of the test chamber volume $V_{test\ chamber}$ the packaging volume $V_{packaging}$ is used.

12 Test report

The test report must contain the following information:

- a) Referral to the technical bulletin;
- b) Nature and description of the test object;
- c) Composition and relative humidity of the oxygen-containing test gas;
- d) Relative humidity of the nitrogen;
- e) For laminated films, the direction of penetration of the O₂ and the relative humidity;
- f) Temperature of the test chamber;
- g) Oxygen permeability calculated using either equation 1 or 2 (see section 12): individual values and the average value;
- h) Any conditions which differ from those specified in this test protocol;
- i) The date of the test.

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Freising, 20.12.2011, Dr. Kajetan Müller, Sven Sänglerlaub, Astrid Pant

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