
International Standard



8008

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Aluminium oxide primarily used for the production of aluminium — Determination of specific surface area by nitrogen adsorption — Single-point method

Oxyde d'aluminium principalement utilisé pour la production de l'aluminium — Détermination de l'aire massique (surface spécifique) par adsorption d'azote — Méthode à un point de mesure

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Foreword

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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 8008 was prepared by Technical Committee ISO/TC 47, *Chemistry*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Aluminium oxide primarily used for the production of aluminium — Determination of specific surface area by nitrogen adsorption — Single-point method

1 Scope and field of application

This International Standard specifies a single-point method for the determination, by nitrogen adsorption, of the specific surface area of aluminium oxide used for the production of metal.

The lower limit is $0,1 \text{ m}^2 \cdot \text{g}^{-1}$.

The upper limit of the present method may be $1\,000 \text{ m}^2 \cdot \text{g}^{-1}$ or greater, but those values are not of interest to the aluminium industry.

The range of measurement depends on the dimensions of the apparatus.

2 References

ISO 803, *Aluminium oxide primarily used for the production of aluminium — Determination of aluminium at 300 °C (conventional moisture)*.

ISO 2927, *Aluminium oxide primarily used for the production of aluminium — Sampling*.

3 Principle

The method is based on the property of the solids to adsorb gas molecules at their surface.

In the range between 0,05 and 0,3 times the saturated vapour pressure of the measuring gas, the multilayer adsorption begins. The formation of the first monolayer of adsorbed molecules can be detected from the behaviour of the adsorption isotherm in this range; this is the only process relevant to the present method.

Nitrogen is introduced at ambient temperature and at atmospheric pressure into two bottles of equal volume one of which contains the test portion while the other is empty. The connected bottles are immersed in refrigerant bath of liquid nitrogen. Since some nitrogen is adsorbed by the sample a differential pressure occurs between the two bottles and is measured by means of a differential manometer. From this difference, the number of molecules adsorbed on the surface is calculated.

This number is multiplied by the known area occupied by a single adsorbed molecule so that the total surface area is obtained. The area occupied by an adsorbed nitrogen molecule is taken as $16,2 \times 10^{-20} \text{ m}^2$.

4 Apparatus

Ordinary laboratory apparatus and

4.1 Adsorption apparatus (see figure 1).

The apparatus consists of a reference bottle (7) and a sample adsorption bottle (8) which are moved onto the two connecting pieces, with sealing rings in between to make the joint gas-tight. At each connecting piece, there is a valve (1 and 2), by which the bottles can be connected to the atmosphere. The measuring gas is admitted to the bottle through the capillaries inside the connecting pieces.

The bottles made of shock-resisting glass have a volume of about 100 cm^3 . The difference between the volume of the two bottles shall not exceed 0,1 %. The bottles' necks consist of calibrated glass tubes with an internal diameter of $9 \pm 0,02 \text{ mm}$. Each tube has an upper and lower mark.

In this way, several bottles can be used as either sample or reference bottles without compensating the volumes for each combination of bottles. A differential manometer containing dibutyl phthalate is arranged between the two bottles. The legs of the differential manometer are connected to the two inlet capillaries of the adsorption bottles. By means of the valve 4, the two bottles, i.e. the two inlet capillaries, can be separated from or connected to each other. By means of the valve 5, the liquid in the two legs of the differential manometer can be separated or connected. The legs of the differential manometer consist of calibrated glass tubes with an internal diameter of $5 \pm 0,02 \text{ mm}$. This ensures that the change in volume during the adsorption measurement can be calculated with sufficient accuracy. The inlet capillary of the sample bottle, being the shorter of the two, is connected to a compensating volume (10), which is adjusted during preparation of the apparatus.

The measuring gas is admitted to the apparatus via the valve 3. If the valves 1, 2 and 4 are open, the measuring gas passes through both bottles. If the valves 1 and 4 are closed, the reference bottle is shut off and only the sample bottle is purged with the measuring gas.

During measurement, only a part of the gas volume, which is downstream of the valve 3 and upstream of the valves 1 and 2, is cooled by liquid nitrogen to the measuring temperature. The gas volume remaining at room temperature shall be limited to 10 % of the total volume at maximum. For this reason, the connections to the adsorption bottles are capillaries, which occupy most of the necks of the bottles in order to keep the portion remaining at room temperature as small as possible.

4.1.1 Adsorption bottle

The adsorption bottle has a calibrated volume of 100 cm³. To facilitate weighing of the sample as well as the cleaning of the adsorption bottle, two-piece bottles are applied. The two pieces are connected by ground joints and fixed by hooks and springs.

4.2 Thermostat, for heating the adsorption bottles in the desorption procedure (6.3) (see figure 2).

4.3 Device for degassing under vacuum (see figure 3).

4.4 Cooling bath, containing boiling nitrogen.

4.5 Water bath, capable of being controlled at 22 ± 3 °C or at approximately 40 °C, as required.

5 Sampling and samples

Sampling shall be carried out in accordance with ISO 2927.

6 Procedure

6.1 Test portion

Choose the mass of sample to be used depending on the supposed specific surface area.

Recommended values are given in table 1.

Table 1

Supposed specific surface area	Mass of sample
m ² .g ⁻¹	g
1	5
5	3
10	2
50	from 0,7 to 1,0
100	from 0,2 to 0,3

NOTE — If the surface area is completely unknown, preliminary tests are necessary to find the best test portion.

6.2 Preparation of apparatus

6.2.1 Checking of new apparatus

New apparatus should be checked to ensure that the compensating volume (10) is adjusted correctly and that the apparatus is gas-tight.

6.2.1.1 Checking the equalization of volumes

The valve 4 (see 6.2.1.2) must be gas-tight when the equalization of the volumes is checked.

Fit the empty adsorption bottles to the connecting pieces; the upper mark on the bottle neck shall coincide with the lower sealing ring. Purge the apparatus with nitrogen by opening all the valves and allowing the gas to flow at approximately 10 l/h. During purging, maintain the bottles immersed in the water

bath (4.5) maintained at 22 ± 3 °C, up to the lower mark on the neck in order to bring them to the same temperature. When the equalization of temperature can be assumed (after at least 5 min), shut off the apparatus from the atmosphere and shut off the two bottles from each another, by closing the valves in the sequence 1, 2, 3 and 4.

On shutting the valve 4, a small pressure difference may appear.

If this pressure difference changes within the next 2 min, a complete temperature equalization has not been reached in the adsorption bottles. In this case, open the valves again in the sequence 4, 3, 2 and 1, and purge the apparatus further with nitrogen. After a few minutes, repeat this check.

If temperature equalization is achieved, close valve 5.

Remove the bottles from the water bath, dry any drops of water adhering to them, and immerse the bottles up to the lower mark in the cooling bath (4.4).

When the bottles have attained the temperature of the boiling nitrogen (with empty bottles after about 1 min), open the valve 5 slowly. If the volumes of the sample and reference sides have been fully equalized, no pressure difference occurs. In this case, close the valve 5 again and open the valve 4. Then remove the cooling bath (4.4) and replace it by the water bath (4.5), maintained at approximately 40 °C, to thaw out the bottles. Remove the warm water bath as soon as the bottles have reached ambient temperature again. After 2 min, reopen the valves 3, 2 and 1 in that sequence, and purge the apparatus with nitrogen. During the cooling and heating of the bottles, great pressure differences may occur momentarily so that the measuring liquid in the manometer may be transferred into other parts of the apparatus. For this reason, do not open the valve 5 before temperature equalization.

If a pressure difference should occur during the preparation of the apparatus, change the compensating volume (10) in such a way that the volumes on both sides of the differential manometer are equal. To check the equalization of the volumes, repeat the test described above.

6.2.1.2 Checking of tightness

If, after the slow opening of valve 5, steadily increasing or very great pressure differences occur (more than 400 mm of liquid column), during the equalization of volume at the temperature of boiling nitrogen, then the apparatus will have a leakage to the atmosphere (for instance, caused by the valves 1, 2, 3). Leakage of valve 4 cannot be recognized by a pressure difference and the following special check shall be carried out. Immerse the bottles in the cooling bath (4.4), close the valves 2, 3 and 4, and open the valves 1 and 5. By means of valve 1, create a pressure difference of approximately 300 mm of liquid column. Close the valve 1.

Within the next 10 min, the liquid column of the differential manometer shall not sink more than 1 mm.

6.2.2 Checking of functioning

When the apparatus is put into operation, and later from time to time, check its functioning by measuring a solid with a known specific surface area. Measure the specific surface area of the test substance by the same method.

6.2.3 Maintenance

Replace the measuring liquid of the differential manometer when it is dirty or at least every year. Change the used drying agent in the drying tower.

6.3 Desorption of samples

Dry the test portion at 300 °C (see ISO 803) and weigh it in the adsorption bottle in such a way that no substance adheres to the wall of the neck.

Evacuate the bottle with the sample three times and purge intermittently with pure nitrogen. Then heat the sample in the thermostat (4.2) for approximately 1 h under vacuum. Keep the vacuum pressure at about 0,01 bar*.

6.4 Adsorption measurement

Open the valves 2 and 3, pass nitrogen through the apparatus and connect the adsorption bottle filled with the pretreated sample and nitrogen to the connecting piece. Then open the valves 1, 4 and 5, and warm the bottles in the water bath (4.5), maintained at approximately 22 °C. After 5 to 10 min, close the valves 1, 2, 3 and 4 and check the sample bottle and the reference bottle for temperature equalization. If a pressure difference appears, reopen the valves in the sequence 4, 3, 2 and 1 and continue purging with nitrogen. When temperature equalization is achieved, close the valve 5 and shut off the nitrogen flow. Immerse the bottles in the cooling bath (4.4) down to the lower mark, and open the valve 5 very slowly. If the existing pressure difference has become constant, read off this difference to an accuracy of 0,5 mm. The time to reach a constant pressure difference may be quite long with some materials, for example those having micropores or a low thermal conductivity. (State in the test report the time interval from immersion of the bottles until reading of the pressure difference.)

After having finished the measurement, close the valve 5 and open the valve 4. Replace the cooling bath (4.4) by the water bath (4.5), maintained at approximately 40 °C. After a few minutes, start the nitrogen flow and open the valves 3, 2, 1 and 5 in that sequence. When the connecting pieces are at ambient temperature, close the valves 1, 4 and 5 and change the sample bottle to carry out a new measurement.

7 Expression of results

7.1 Equations

The specific surface area S_m , is given by the following equation :

$$S_m = 1,05 \frac{N_L \sigma_{N_2} (p_o - p)}{m R p_o} \left[\frac{V \Delta p}{T_k} + \frac{V_z \Delta p}{T_z} + \frac{2V_x p}{T_z} + \frac{V_x \Delta p}{T_z} \right] + 1,05 \frac{N_L \sigma_{N_2} (p_o - p) V_P}{m R p_o} \left[\frac{p}{T_k} - \frac{p_B}{T_z} \right] \dots (1)$$

where the symbols are as defined in table 3.

In this equation, the single-point calculation of the BET equation has been assumed and the correcting factor of 1,05 which represents the density of the liquid in the differential

manometer introduced. For practical purposes, σ_{N_2} , V , V_z , T_k , p_o have been taken as constants. In addition, the expression $V_z \Delta p / T_z$ is small compared with the other terms of the sum in the first square brackets and has been neglected.

Incorporating the numerical values and units given in table 3, the following numerical equation is obtained with $T_z = 295$ K for calculating the mass-related surface area :

$$S_m = 1,1736 \times 10^3 (1,05 - p) \frac{\Delta h}{m} (1,3693 \times 10^{-4} + 6,655 \times 10^{-5} p) + 1,1736 \times 10^3 (1,05 - p) \frac{V_P}{m} \left(\frac{p}{77,6} - \frac{p_B}{295} \right) \dots (2)$$

The second V_P -containing term of the sum of this equation can be neglected, if the specific surface areas S_m are $> 10 \text{ m}^2 \cdot \text{g}^{-1}$. The equilibrium pressure p in equation (2) is calculated according to the following unit equation :

$$p = \frac{V + V_z}{\frac{T_z}{T_k} + V_z + V_x} p_B - \Delta p \dots (3)$$

where

$$\Delta p = \rho g \Delta h \dots (4)$$

For practical purposes, T_k , ρ and $V_x = \frac{\pi r^2 \Delta h}{2}$ ($\approx 1 \text{ cm}^3$ at $\Delta h = 100 \text{ mm}$) are taken as constants. Incorporating the numerical values and units given in table 3, the following numerical equation is obtained at $T_z = 295$ K :

$$p = 0,278 p_B - 1,025 \times 10^{-4} \Delta h \dots (5)$$

If T_z deviates from $T_z = 295$ K by more than ± 3 K, the two constants in equations (2) and (5) have to be corrected and the actual room temperature T_z must be taken into account :

$$S_m = 1,1736 \times 10^3 \frac{(1,05 - p)}{m} \left[\Delta h (1,3693 \times 10^{-4} + B_1 p) + V_P \left(\frac{p}{T_k} - \frac{p_B}{T_z} \right) \right] \dots (6)$$

$$p = B_2 p_B - 1,025 \times 10^{-4} \Delta h \dots (7)$$

Incorporating the numerical values and units given in table 3, one obtains for B_1 and B_2 :

$$B_1 = \frac{2V_x}{\Delta h T_z} = 1,9635 \times 10^{-2} \frac{1}{T_z} \dots (8)$$

$$B_2 = \frac{V + V_z}{V \frac{T_z}{T_k} + V_z + V_x} = \frac{109,550}{1,304 T_z + 9,332} \dots (9)$$

where the symbols and constants used have the meanings shown in table 3.

7.2 Calculation by means of a nomogram

The calculation may be simplified using the nomogram indicated in figure 4.

* 1 bar = 10^5 Pa

Table 2
 $B_1, B_2 = f(T_z)$

T_z (K)	$B_1 \times 10^5$	$B_2 \times 10$
291	6,747	2,817
292	6,724	2,807
293	6,701	2,798
294	6,678	2,789
295	6,656	2,780
296	6,633	2,770
297	6,611	2,761
298	6,588	2,752
299	6,566	2,743
300	6,544	2,734
301	6,523	2,725
302	6,501	2,717
303	6,480	2,708
304	6,458	2,699
305	6,437	2,691
306	6,416	2,682
307	6,395	2,673
308	6,374	2,666

Knowing the atmospheric pressure and the pressure difference read off on the differential manometer, the factor A is taken from the nomogram (see figure 4).

The specific surface area of the sample, expressed in square metres per gram, is given by the formula

$$S_m = \frac{A \Delta h}{m}$$

where

Δh is the pressure difference, in millimetres;

m is the mass, in grams, of the test portion.

The nomogram allows the calculation of specific surface area in the range between 10 and 300 $\text{m}^2 \cdot \text{g}^{-1}$ approximately.

For values less than 10 $\text{m}^2 \cdot \text{g}^{-1}$ or greater than 300 $\text{m}^2 \cdot \text{g}^{-1}$, which are generally not of interest in the aluminium industry, use equations (6) and (7) for the calculation.

7.3 Precision

Repeatability : $\pm 0,5 \%$

Reproducibility : $\pm 1 \%$

Table 3

Symbol	Quantity	Unit
S_m	Mass-related surface area	$\text{m}^2 \cdot \text{g}^{-1}$
p	Equilibrium pressure	bar
Δh	Difference in height on the differential manometer	mm
V_p	Volume of the solid sample	cm^3
m	Mass of the test portion	g
p_B	Filling pressure (atmospheric pressure)	bar
p_o	Saturation pressure of boiling nitrogen ($p_o = 1,05$ bar)	bar
N_L	Loschmidt number, Avogadro constant ($N_L = 6,023 \times 10^{23} \text{ mol}^{-1}$)	mol^{-1}
R	Molar gas constant ($R = 8,314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
ρ	Density of dibutyl phthalate = 1,05 $\text{g} \cdot \text{cm}^{-3}$	$\text{g} \cdot \text{cm}^{-3}$
g	Acceleration of free fall ($g = 981 \text{ cm} \cdot \text{s}^{-2}$)	$\text{cm} \cdot \text{s}^{-2}$
σ_{N_2}	Area occupied by a nitrogen molecule ($\sigma_{N_2} = 16,2 \times 10^{-20} \text{ m}^2$)	m^2
V	Volume of the adsorption bottle, into which the capillary is introduced, up to the level of the cooling bath ($V = 101,2 \text{ cm}^3$)	cm^3
V_z	Volumes of the sample part and the reference part from the level of the cooling bath to the zero level of the differential manometer. (These volumes remain at room temperature during measurement.) ($V_z = 8,35 \text{ cm}^3$)	cm^3
V_x	Change of volume in one leg of the differential manometer during measurement	cm^3
r	Internal radius of the tube of the differential manometer ($r = 0,25 \text{ cm}$)	cm
T_K	Temperature of the cooling bath (4.4) ($T_K = 77,6 \text{ K}$)	K
T_z	Ambient temperature and temperature of the water bath (4.5)	K
Δp	Pressure difference	bar
B_1 B_2	} Abbreviations, see equations (8) and (9)	

8 Test report

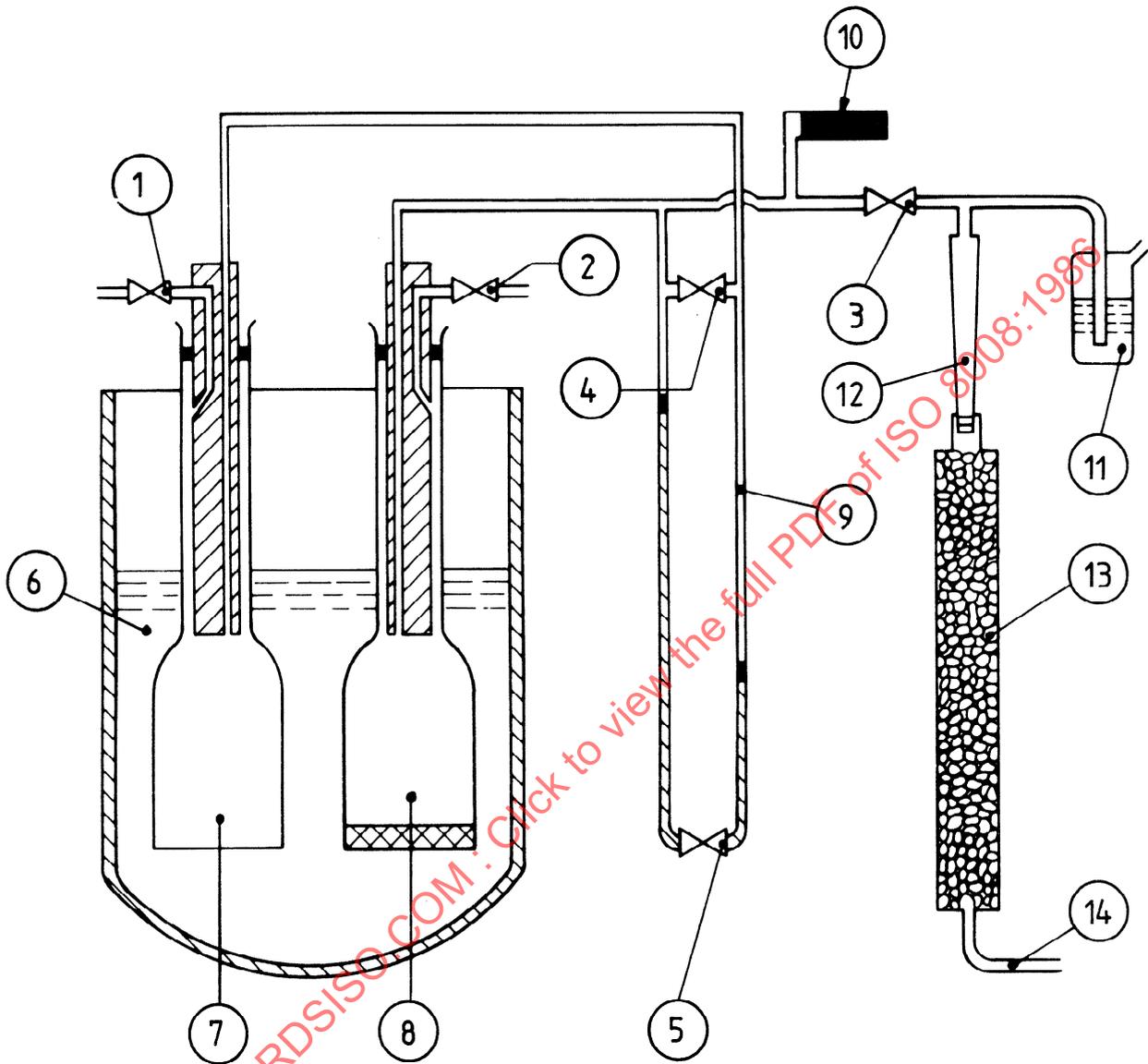
The report shall include the following particulars :

- a) the laboratory, operator, and date of test;
- b) an identification of the sample;
- c) the reference of the method used;
- d) pre-treatment of the sample : temperature and time of preliminary drying, temperature and time of desorption heating, application of nitrogen or of vacuum during desorption heating;
- e) the atmospheric pressure during the measurement, temperature of the water bath during the measurement, time from immersion of the adsorption bottles in the cooling bath until reading of the pressure difference;
- f) the difference in height which is read off at the differential manometer;
- g) the specific surface area of the sample, or, if desired, the mean value and its standard deviation;
- h) any unusual features noted during the determination;
- i) any operation not included in the International Standard or in the International Standards to which reference is made, or regarded as optional.

9 Bibliography

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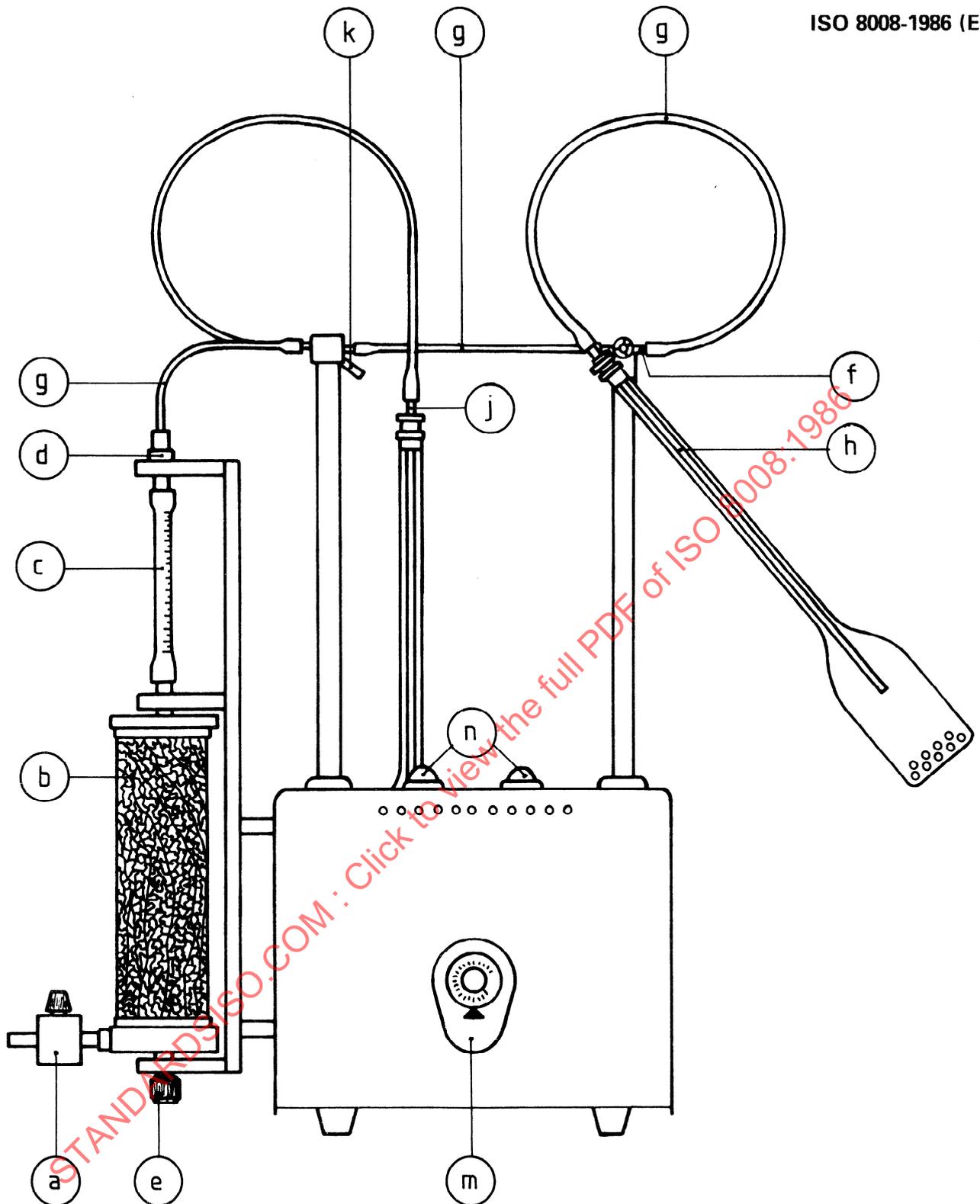
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|--------|------------------------|---|---------------------|
| ① to ⑤ | Valves | ⑩ | Compensating volume |
| ⑥ | Cooling bath | ⑪ | Control bottle |
| ⑦ | Reference bottle | ⑫ | Flowmeter |
| ⑧ | Sample bottle | ⑬ | Drying tower |
| ⑨ | Differential manometer | ⑭ | Nitrogen inlet |

Figure 1 — Areameter adsorption apparatus



- | | |
|--|--|
| (a) Inlet valve for the measuring gas (nitrogen) | (g) Connecting hose |
| (b) Drying cylinder | (h) Purging capillary (not necessary for the two-piece bottle) |
| (c) Flowmeter | (j) Plug with hole and holding device |
| (d) Connecting piece | (k) Holding pins |
| (e) Locking screw | (m) Temperature controller |
| (f) Outlet for measuring gas | (n) Control lights |

Figure 2 — Thermostat for the heating of the adsorption bottles in the desorption procedure