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Nuclear fuel technology — Guidelines on the measurement of the specific surface area of uranium oxide powders by the BET method

Technologie du combustible nucléaire — Lignes directrices pour le mesurage de l'aire massique (surface spécifique) des poudres d'oxyde d'uranium par la méthode BET

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Foreword

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This document was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection*, Subcommittee SC 5, *Nuclear installations, processes and technologies*.

This second edition cancels and replaces the first edition (ISO 12800:2003), which has been technically revised.

Nuclear fuel technology — Guidelines on the measurement of the specific surface area of uranium oxide powders by the BET method

1 Scope

This document gives guidelines on the determination of the specific surface area of as-fabricated uranium dioxide powder by volumetric or gravimetric determination of the amount of nitrogen adsorbed on the powder, and can be applied to other similar materials, e.g. U_3O_8, UO_2-PuO_2 powders, and other bodies with similar surface areas, e.g. powder granules or green pellets, provided that the conditions described are fulfilled. Modifications using other adsorbing gases are included.

The method is relevant as long as the expected value is in the range between 1 m^2/g and 10 m^2/g.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at http://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

4.1 Summary of the BET method

The BET method is based on the determination of the amount of gas necessary to cover the surface by a monomolecular layer. This amount is determined from the isothermal adsorption curve of nitrogen (N_2) at the temperature of liquid nitrogen (77,4 K) according to Reference [2]. The amount of N_2 adsorbed at a given pressure is determined by volumetric or gravimetric measurement[6]. In order to remove surface contamination of the adsorbent, the sample has to be evacuated and heated under appropriate conditions before the measurement is performed.

4.2 Isothermal adsorption curves

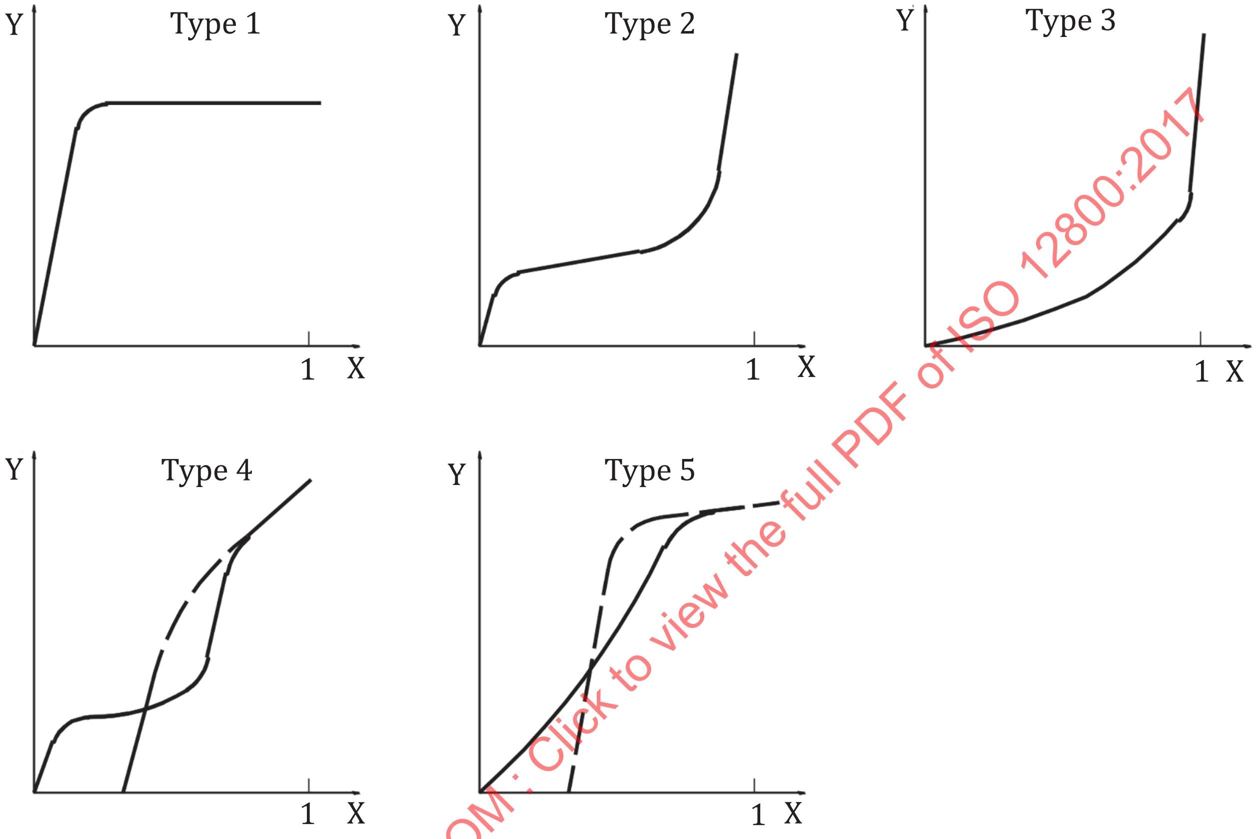
The isothermal adsorption curve describes the relationship between the mass of the adsorbate, m_A (N_2), adsorbed per gram of adsorbent (e.g. UO_2 powder) at an equilibrium pressure of p at constant temperature T, as shown in Formula (1):

$$m_A = f(p,T) \tag{1}$$

Generally, the relative pressure p/p_0 is introduced instead of the absolute pressure p, where p_0 is the saturation vapour pressure which is 1,013 × 10^5 Pa for nitrogen at 77,4 K.

Most isothermal adsorption curves can be classified according to Reference [3] to be one of the five common types (see Figure 1).

Materials with pure micropores (<2 nm diameter) result in a type 1 adsorption curve. Most frequently, types 2 and 4 adsorption curves are observed where the adsorption energy of the first layer, E_1, is much higher than that of subsequent layers, E_n. When $E_1 \approx E_n$, type 3 or type 5 adsorption curves result. The BET method can be applied to type 2 and type 4 curves only. The practice shows that the UO_2, U_3O_8 and PuO_2 powders meet this condition.



Key

X	relative pressure
Y	specific amount adsorbed
Type 1	Langmuir type
Type 2	adsorption followed by condensation
Type 3	condensation type
Type 4	two-fold adsorption
Type 5	condensation followed by adsorption

Figure 1 — Classification of adsorption isotherms

4.3 Conditions and assumptions

The method can only be applied to materials where

a) nitrogen is not absorbed by the material,

b) nitrogen does not react chemically with the adsorbent,

c) all pores can be reached by the nitrogen molecule, and

d) a type 2 or type 4 adsorption curve is observed.

The BET theory includes the following assumptions.

- The adsorption energy of the first layer is independent of the degree of occupation. The adsorption energy as well as the kinetic parameters and condensation/evaporation equilibrium conditions for the second and higher layers are equal.
- The probability of adsorption at a vacant site is independent of the occupation of the neighbouring sites.
- Horizontal interactions between the adsorbed N_2 molecules can be neglected.
- The heterogeneity of the adsorbent surface can be neglected.

5 Procedure

5.1 Sample preparation

Impurities on the sample surface, especially water vapour, shall be removed before the adsorption measurement. Conditions for removing impurities (vacuum, temperature, time) have to be found which are compatible with the powder type. Chemical reactions (decomposition), sintering, change of crystal structure and other processes on the surface shall be avoided. Long evacuation periods are needed for highly porous powders. In order to shorten the heating time, the optimum temperature should be determined. In most cases, the measured specific surface area first increases with an increase in the heating temperature and then decreases, e.g. by sintering of the powder.

The optimum pre-treatment of hyperstoichiometric UO_2 powder depends on its specific surface area, intra-particle open pore size, and stoichiometry. For powders with a specific surface area between 2 m^2/g and 8 m^2/g, evacuation down to 2 mPa to 10 mPa (10^{-5} Torr to 10^{-4} Torr) followed by heating for 2,5 h at (150 °C ± 10 °C) is sufficient. Equivalent conditions, like 1,5 h at (180 °C ± 10 °C) or others, can be utilized as well. To prevent sintering, heating temperatures higher than 350 °C should be avoided if the O to U ratio exceeds 2,10. Shorter heating times to 20 min are possible. Instead of evacuation, the powder can be purged with purified inert gas at the temperatures and for the times mentioned above after having verified that there is no deleterious effect on characteristics of powders.

Mass of sample required depends upon material density and expected specific surface area.

5.2 Volumetric measurement

The pre-treated sample of known mass is placed in a bulb of calibrated volume, which is filled with nitrogen at a defined temperature and pressure. At ambient temperature and pressure, measurable adsorption does not occur. The closed bulb is cooled to the temperature of liquid nitrogen. The adsorbed amount of nitrogen can be calculated from the amount of nitrogen enclosed in the bulb, the volume, the temperature, and the pressure drop. Accurate volumetric measurements[4][5] can be obtained by measuring the difference in pressure between the sample-containing bulb and an empty reference bulb.

5.3 Gravimetric measurement

In this case, the nitrogen is adsorbed at constant temperature and pressure. The amount of nitrogen adsorbed is directly measured by means of a microbalance.

5.4 Original and single-point methods

The determination of the specific surface area requires the static volumetric or gravimetric measurement of at least three data points of the adsorption curve in the relative pressure region $0,05 < p/p_0 < 0,35$. The measurements shall be made under equilibrium conditions.

If less accuracy is acceptable, the determination can be made easier by application of the single-point method, taking only one point of the adsorption curve in the relative pressure range $0{,}05 < p/p_0 < 0{,}35$ ("single-point method").

5.5 Dynamic method (carrier gas method)

The BET method may also be applied in a dynamic, flowing gas system. The relative pressure of the adsorbing gas (p/p_0) is obtained by mixing with an inert gas, usually helium. A stream of this gas mixture is passed over the sample which is cooled to 77,4 K in liquid nitrogen. Nitrogen from the gas stream is adsorbed on the sample.

On warming the sample to ambient temperature, the adsorbed nitrogen is desorbed into the gas stream. The amount of nitrogen desorbed is detected using a katharometer coupled to an integrator. The katharometer is calibrated by an injection of pure nitrogen.

5.6 Alternative methods

Modified methods use other adsorptives and other temperatures (see Table 1). The occupied areas per adsorbed molecule (or atom in the case of argon, krypton, and xenon) are also reported in Table 1.

Another indirect method is the tracer method[8][9], where the amount of a radioactive adsorbed gas is determined by activity measurements.

Table 1 — Occupied areas per adsorbed molecule

Gas	Temperature K	Saturation pressure, p_0 Pa	Occupied area[a] per molecule nm^2
Nitrogen	77,4	$1{,}01 \times 10^5$	0,162
Argon	77,4	$2{,}58 \times 10^4$	0,138
Argon	87,3	$1{,}33 \times 10^5$	0,142
Krypton	77,4	$2{,}66 \times 10^2$	0,202
Krypton	90,2	$2{,}27 \times 10^2$	0,214
Xenon	90,2	8,00	0,232

[a] Standard values.

6 Expression of results

6.1 Methods of calculation

6.1.1 Multipoint determination

The so-called BET equation is given by Formula (2):

$$V_A = \frac{V_m \cdot C \cdot p_r}{(1 - p_r)(1 - p_r + C \cdot p_r)} \qquad (2)$$

where

V_A is the adsorbed gas volume [standard temperature and pressure (S.T.P.)] at the relative pressure on unit mass of sample, in $cm^3\ g^{-1}$;

$p_r = p/p_0$ p_r is the relative pressure, p_0 is the saturation vapour pressure at the temperature of measurement;

V_m is the gas volume (S.T.P.) needed for a complete monolayer on unit mass of sample, in $cm^3\ g^{-1}$;

C is a parameter of kinetics. $\left[C = \exp\left(\frac{E_1 - E_l}{RT}\right)\right]$

where

E_1 is the adsorption energy;

E_l is the liquefaction energy.

Rearrangement of Formula (2) yields Formula (3):

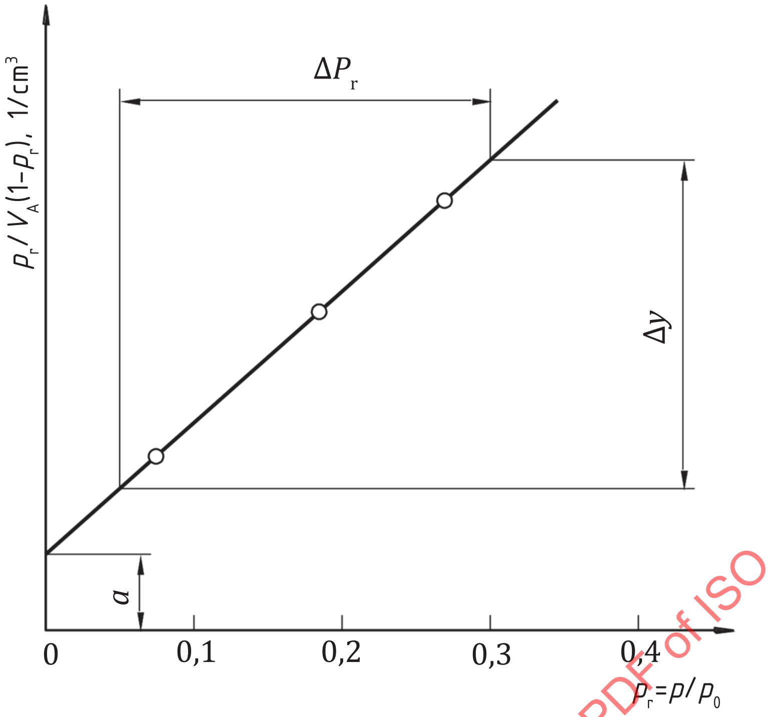
$$\frac{p_r}{V_A(1-p_r)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} p_r \qquad (3)$$

Formula (3) is the formula of a straight line $y = a + bx$ obtained by linear regression with Formula (4):

$$a = \frac{1}{V_m C} \text{ and } b = \frac{C-1}{V_m C} \qquad (4)$$

If $p_r/V_A\ (1 - p_r)$ is plotted as a function of p_r, one obtains the so-called BET line (see Figure 2). From Formula (4) follows Formula (5):

$$V_m = \frac{1}{a+b} \text{ and } C = \frac{b}{a} + 1 \qquad (5)$$



$$y = a + b \cdot p_r$$

$$a = 1 / (V_m C)$$

$$b = \Delta y / \Delta P_r = (C - 1) / (V_m C)$$

NOTE The symbols are defined in 6.1.1.

Figure 2 — The BET line

The parameters a and b can be obtained by calculation, as well as by graphical determination. The specific surface area, S_m (volumetric method), is determined by Formula (6):

$$S_m = \frac{v_m \cdot N_A}{m \cdot v_A} \cdot f \tag{6}$$

where

m is the mass of the adsorbent in g (e.g. UO_2 powder);

N_A is the Avogadro number ($6{,}023 \times 10^{23} \cdot \mathrm{mol}^{-1}$);

v_m is the volume (S.T.P) of the adsorbate required for making a monolayer on the powder surface, in cm^3;

v_A is the molar volume of adsorbate gas (S.T.P.) in $\mathrm{cm}^3\ \mathrm{mol}^{-1}$;

f is the occupied area per adsorbed molecule in m^2 (see Table 1).

When the capacity of the monolayer is determined as the mass of adsorbate (gravimetric method), the specific surface area yields Formula (7):

$$S_m = \frac{m_m \cdot N_\mathrm{A}}{m \cdot M} f \tag{7}$$

where

m_m is the mass of the adsorbate,

M is the molar mass of the adsorbate.

6.1.2 Single-point determination

The specific surface area can be determined by a single point measurement if $C \gg 1$ (preferably $C \geq 100$) and $1/C < p/p_0$. Formula (2) is simplified to Formula (8):

$$V_m = V_\mathrm{A}(1 - p_\mathrm{r}) \tag{8}$$

6.2 Precision and accuracy

The precision of this method depends on the particular equipment used for the measurement.

As mass of sample needed depends upon material density and expected specific surface area, the user is responsible for determining accuracy and precision as part of their method qualification process.

The apparatus should be periodically calibrated using a certified reference material such as those proposed in ISO 9277.

7 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 12800:2017;

b) all data necessary for identification of the sample;

c) results of the test, expressed as the measure with units of measure and the expanded uncertainty with the appropriate coverage factor, calculated in accordance with JCGM 100 (ISO/GUM);

d) location and date of the test;

e) certified or working reference material(s) used for performance testing of the instrument and validation of results;

f) the following procedural measurement details have to be reported:

  - method of degassing; heating conditions;
  - test method; apparatus and calculation method used;
  - adsorbate (including purity);
  - measurement temperature.