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

Technologie du combustible nucléaire — Principe de la mesure 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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Nuclear fuel technology — Guide to the measurement of the specific surface area of uranium oxide powders by the BET method

1 Scope

This International Standard covers 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.

2 Principle

2.1 Summary of the method

The 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 at the temperature of liquid nitrogen (77,4 K) according to Brunauer, Emmett and Teller (BET) [1] since the adsorbate N_2 is physically adsorbed on the adsorbent. The amount of N_2 adsorbed at a given pressure is determined by volumetric or gravimetric measurement. 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.

2.2 Isothermal adsorption curves

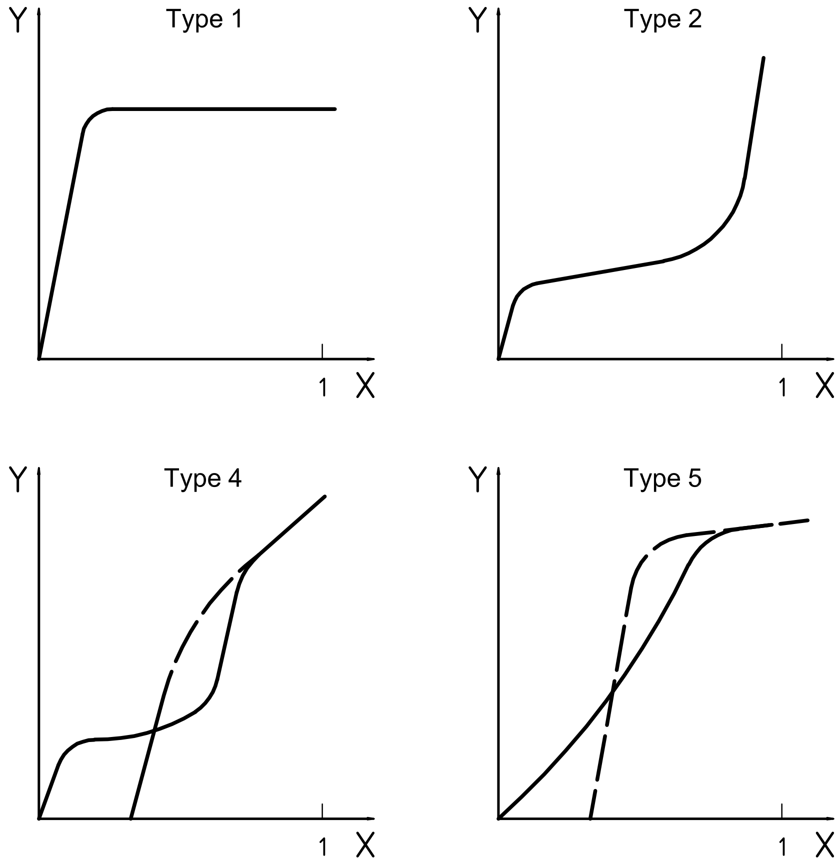
The isothermal adsorption curve describes the relationship between the mass of the adsorbate m_A (N_2) adsorbed per gram of adsorbent (e.g. UO_2 powder) at an equilibrium pressure of p at constant temperature T:

$$m_\mathrm{A} = f(p,T) \tag{1}$$

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 Brunauer, Deming L., Deming W. and Teller [2] 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, type 2 and 4 adsorption curves are observed where the adsorption energy of the first layer E_1 is much higher than that of the higher 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.



Key

X relative pressure

Y specific amount adsorbed

Type 1 Langmuir type

Type 2 Adsorption followed by condensation

Type 3 Condensation type

Type 4 Twofold adsorption

Type 5 Condensation followed by adsorption

Figure 1 — Classification of adsorption isotherms

2.3 Conditions and assumptions

The method can only be applied to materials where

a) nitrogen is not absorbed in the matrix,

b) nitrogen does not react chemically with the adsorbent,

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

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

The BET theory includes the following assumptions:

1) 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.

2) The probability of adsorption at a vacant site is independent of the occupation of the neighbouring sites.

3) Interactions between the adsorbed N_2 molecules as well as the heterogeneity of the adsorbent surface can be neglected.

3 Procedure

3.1 Sample preparation

Impurities on the sample surface, especially water vapour, must 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 must 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 pretreatment of hyperstoichiometric UO_2 powder depends on its specific surface area, intra particle open pore size, and stoichiometry. To reach the precision described in 4.2 for powders with a specific surface area between 2 and 8 m^2/g, evacuation down to several mPa (10^{-5} to 10^{-4} Torr) followed by heating for 2,5 h at (150 ± 10) °C is sufficient. Equivalent conditions, like 1,5 h at (180 ± 10) °C or others, can be utilized as well. To prevent sintering, heating temperatures higher than 350 °C should be avoided if the O:U ratio exceeds 2,10. Shorter heating times down to 20 min are possible if the powder-particle pore structure is appropriate. 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.

3.2 Volumetric measurement [3, 4]

The pretreated sample of known mass is 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 down 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 can be obtained by measuring the difference in pressure between the sample-containing bulb and an empty reference bulb.

3.3 Gravimetric measurement [5]

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.

3.4 Original and single-point methods

A complete accurate determination of the specific surface area requires the discontinuous volumetric or gravimetric measurement of at least three data points of the adsorption curve in the relative pressure region $0{,}05 \le p/p_0 \le 0{,}35$. The measurements must 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 $0{,}05 \le p/p_0 \le 0{,}35$ (“Single-point method”).

3.5 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.

3.6 Alternative methods

Modified methods use other adsorbtives 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 [7, 8], where the amount of a radioactive adsorbed gas is determined by activity measurements.

Table 1 — Occupied areas per adsorbed molecule

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

[a] The bath temperature depends on the purity of the liquid and on the barometric pressure.

[b] Standard values.

4 Expression of results

4.1 Methods of calculation

4.1.1 Multipoint determination

The so-called BET equation is given by

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

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_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 Adsorption energy

E_l Liquefaction energy

Rearrangement of Equation (2) yields:

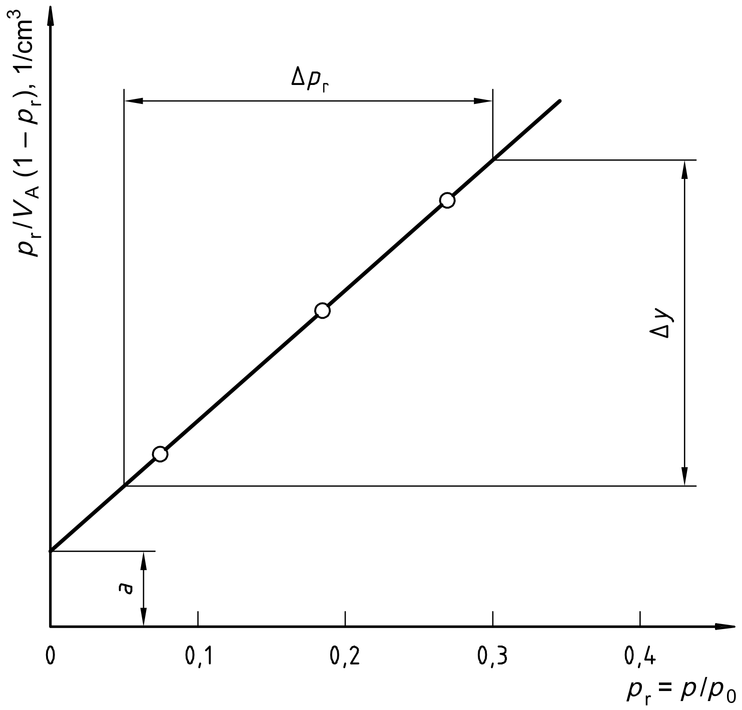
$$\frac{p_{\mathrm{r}}}{V_{\mathrm{A}}\left(1 - p_{\mathrm{r}}\right)} = \frac{1}{V_{\mathrm{m}}C} + \frac{C-1}{V_{\mathrm{m}}C}\, p_{\mathrm{r}} \tag{3}$$

Equation (3) is the equation of a straight line $y = a + bx$ with

$$a = \frac{1}{V_{\mathrm{m}}C} \text{ and } b = \frac{C-1}{V_{\mathrm{m}}C} \tag{4}$$

If $p_{\mathrm{r}}/V_{\mathrm{A}}\ (1 - p_{\mathrm{r}})$ is plotted as a function of p_{r}, one obtains the so-called BET line (see Figure 2). From Equation (4) it follows that

$$V_{\mathrm{m}} = \frac{1}{a+b} \text{ and } C = \frac{b}{a} + 1 \tag{5}$$



$y = a + b \cdot p_{\mathrm{r}}$

$a = 1 / (V_{\mathrm{m}}C)$

$b = \Delta y / \Delta P_{\mathrm{r}} = (C - 1) / (V_{\mathrm{m}}C)$

NOTE The symbols are defined in 4.1.1.

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:

$$S_m = \frac{V_m \cdot N_A}{m \cdot V_A} f \qquad (6)$$

where

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

N_A is the Avogadro number (6,023 10^{23} 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

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:

$$S_m = \frac{m_m \cdot N_A}{m \cdot M} f \qquad (7)$$

where

m_m is the mass of the adsorbate

M is the molar mass of the adsorbate

4.1.2 Single-point determination

The specific surface area can be determined by a single point measurement if C@1 (preferably C ≥ 100) and $1/C < p/p_0$. Equation (2) is simplified to:

$$V_m = V_A(1 - p_r) \qquad (8)$$

4.2 Precision

The precision of this method depends on the particular equipment used for the measurement. On uranium dioxide powders in the range between 1 and 10 $m^2 \cdot g^{-1}$, a relative standard deviation of ± 2 % can be obtained when the volumetric multipoint measurement with nitrogen at the temperature of the liquid nitrogen is performed.

5 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all data necessary for identification of the sample;

c) results of the test;

d) location and date of the test.

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.

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