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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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ISO 12800 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

# 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

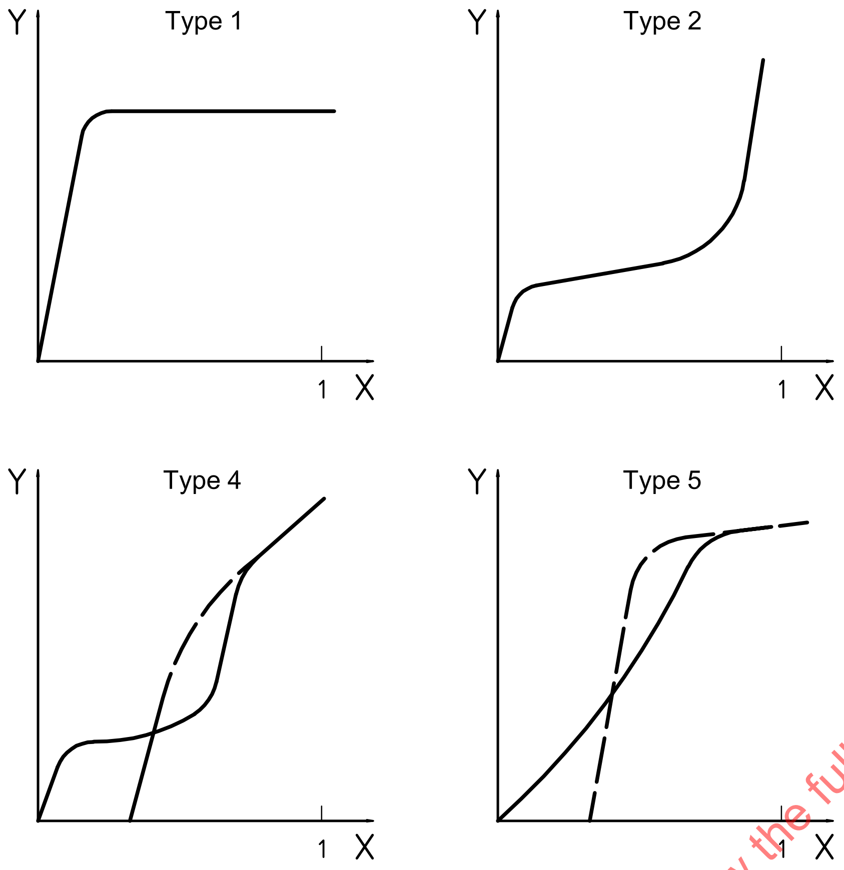
The isothermal adsorption curve describes the relationship between the mass of the adsorbate $m_A$ ($N_2$) adsorbed per gram of adsorbent (e.g. $UO_2$ powder) at an equilibrium pressure of $p$ at constant temperature $T$:

$$m_A = f(p,T) \qquad (1)$$

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 adsorbed amount
Y relative pressure

| | |
|---|---|
| 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 adsorbed 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, pore structure, 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 hrs 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.

### 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 $0{,}05 \leqslant p/p_0 \leqslant 0{,}35$. 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 $0{,}05 \leqslant p/p_0 \leqslant 0{,}35$ ("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 (S.T.P.) at the relative pressure;

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

$V_m$ is the gas volume (S.T.P.) needed for a complete monolayer;

$C$ is a parameter of kinetics.

Rearrangement of Equation (2) yields:

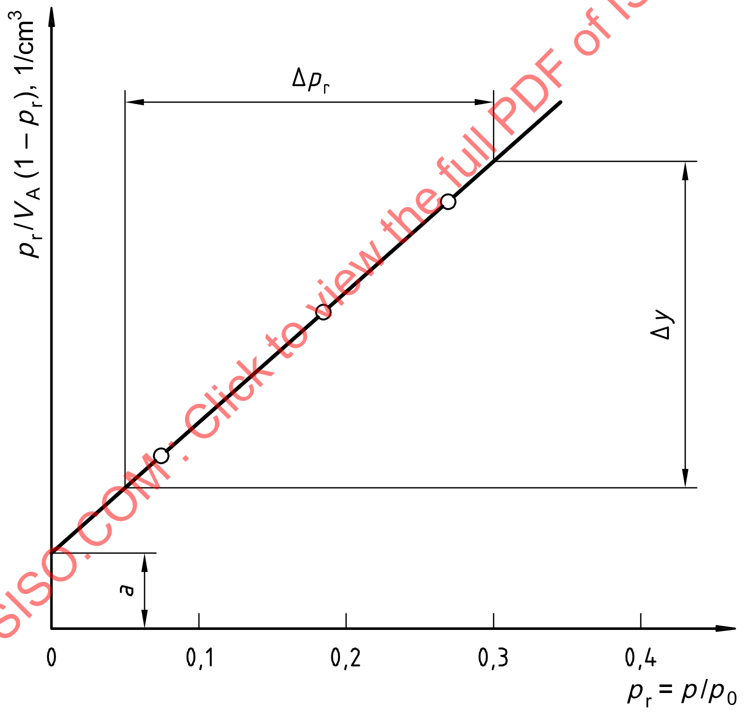
$$\frac{p_{\mathrm{r}}}{V_{\mathrm{A}}\left(1-p_{\mathrm{r}}\right)}=\frac{1}{V_{\mathrm{m}}C}+\frac{C-1}{V_{\mathrm{m}}C}\,p_{\mathrm{r}} \qquad (3)$$

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

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

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

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



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

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

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

NOTE The symbols are defined in 4.1.1.

**Figure 2 — The BET line**