Estimating the uncertainty of the specific surface area of Titanium Oxide Nanotubes calculated from nitrogen adsorption isotherms

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Abstract. The characterization of the textural properties of porous solids by isotherms of adsorption-desorption of nitrogen is a procedure commonly used for the study of the porosity of a solid, which is a great importance for meso and microporous solid materials. In the present work an analysis of the estimate the uncertainty associated to the calculation of the specific surface area was carried out. Here, the specific surface area of titanium oxide nanotubes was determined from N2 adsorption isotherms data. The number of moles of gas adsorbed per gram of adsorbent were the input quantities with higher contribution to uncertainty of the surface area.

1. Introduction

An area of active research is the production of one-dimensional nanostructures, such as nanotubes, nanoribbons and nanorods, because they exhibit interesting optical, magnetic or chemical properties as a result of their small size. Some of the most relevant properties of the aforementioned nanostructures are the high mobility of electrons, high specific surface and quantum confinement effects. As a result, the exploration of new materials based on nanostructures made up of new materials, such as the inorganic nanotubes of metal sulfides and oxides, has grown. Titanium dioxide is one of the compounds used to create nanostructures used in photocatalysis, solar cells and medical devices, among others, due to its high chemical stability, low cost, high area-volume ratio and high surface activity [1].

The nitrogen adsorption characterization is the most used method to evaluate the textural properties of the adsorbents. The specific surface area represents the surface per unit mass of a solid, which has an important effect on the physicochemical interactions between adsorbent and adsorbate. An appropriate determination of the surface area depends of the adequate measurement of N2 adsorption-desorption isotherms at 77 K, and its correct physical interpretation. A good use of the measurements requires the estimation of the level of doubt or uncertainty that it possess. The process of uncertainty
estimation also allows to obtain information about the sources that have higher contribution to the uncertainty of the result of a measurement. Taking into account the above considerations, the present work is focused on the analysis of the uncertainty of the specific surface area of adsorbent materials, determined from isotherms of nitrogen adsorption of samples nanotubes of TiO₂ (TiNTs) prepared by a hydrothermal method.

2. Materials and methods

Materials

Two samples of TiNTs were prepared using a hydrothermal process in an autoclave reactor under autogenous pressure. The temperatures of 383.15 K and 393.15 K were used for the hydrothermal process, anatase nanopowder (Sigma Aldrich) and a solution 10 M of NaOH were used as precursors [2].

Equipment

3FLEX Surface Characterization Analyzer Micrometrics was used for the adsorption measurements. It operates on the basis of a volumetric method, establishing the volume of N₂ adsorbed at the boiling temperature of the liquid nitrogen (77 K) as a function of the equilibrium pressure. The samples were degassed previously during 12 h at 383 K.

Mathematical model

The uncertainty estimation was performed using the procedure described in the Guide for Uncertainty Estimation (GUM method) [3]. The software Microsoft Excel was used to perform the calculations.

The specific surface area was determined using the BET method [4], which is based on the following Langmuir assumptions: (1) all adsorption centers are equivalent, (2) the adsorption capacity of a center is not affected by the occupation in the adjacent centers, and (3) each center can adsorb several layers of molecules. The measurement model of the BET method is represented in Figure 1.

![Figure 1. Model of measurement of specific surface area. The input quantities are presented in circles.](image-url)
Where $N_A$ is Avogadro number, $M_N$ is the molar mass of nitrogen, $Acs$ is the cross-sectional area of the nitrogen molecule, $\rho_{STP}^u$ is the density of the nitrogen vapor at standard temperature and pressure, $n_m$ is the number of moles of gas adsorbed per gram of the adsorbent, $P^D$ is the standard saturation pressure, $P$ is the adsorptive pressure, and $S_{BET}$ is the specific surface area of the adsorbent.

Applying the GUM method, the calculation of the surface area uncertainty is described by Equation (1).

$$
\begin{align*}
\frac{u^2(S_{BET})}{S_{BET}} &= \left(\frac{\partial S_{BET}}{N_A}\right)^2 u^2(N_A) + \left(\frac{\partial S_{BET}}{M_N}\right)^2 u^2(M_N) + \left(\frac{\partial S_{BET}}{Acs}\right)^2 u^2(Acs) + \left(\frac{\partial S_{BET}}{\rho_{STP}^u}\right)^2 u^2(\rho_{STP}^u) \\
&+ \sum_{k=1}^{n} \left(\frac{\partial S_{BET}}{n_{a,k}}\right)^2 u^2(n_{a,k}) + \sum_{k=1}^{n} \left(\frac{\partial S_{BET}}{P_k}\right)^2 u^2(P_k)
\end{align*}
$$

[Equation 1]

3. Results

3.1 Adsorption isotherms

The determination of the surface area of the evaluated samples was obtained through an adsorption analysis. In this technique, the solid material is contacted with a gas (N2), and the pressure is gradually increased in the system until the solid surface reach its nitrogen saturation pressure. As the pressure increases, nitrogen molecules are adsorbed on the surface of the nanotubes to complete a monomolecular layer at a constant temperature. If the pressure continues increasing, a multi-layer adsorption and smaller pore filling are generated, resulting in capillary condensation. In the Figure 2 shows the adsorption isotherms obtained from the samples of TiNTs prepared. According to the classification of IUPAC, the isotherms correspond to a class IV, which is characteristic of the mesoporous adsorbents with weak affinity [5].

Figure 2. Adsorption isotherms of TiO2 nanotubes, prepared by a hydrothermal process (A) TiNTs at 383.15 K and (B) TiNTs 393.15 K
The appearance of the hysteresis cycle (adsorption - desorption) is due to a process of capillary condensation in the pore of mesoporous materials [5].

3.2 Estimation of measurement uncertainty

Analysis of the uncertainty of properties measured at very small scale is important in determining whether the process of preparation of nanostructures is appropriate [6]. From the mathematical model proposed for the determination of the surface area indicated in figure 1, the sources of uncertainty associated with the measurement process were identified, and the quantification of each one of the uncertainties that came from the sources identified as shown in Table 1. The uncertainty values differ for each of the evaluated samples.

| Sample 1 TiNTs | Sample 2 TiNTs |
|----------------|----------------|
| **Input quantities** | **Uncertainty u(i)** | **Input quantities** | **Uncertainty u(i)** |
| $P_1$ [mmHg] | 0.0019 | $n_{a1}$ [mol] | 1.89 | $P_1$ [mmHg] | 0.0013 | $n_{a2}$ [mol] | 1.37 |
| $P_2$ [mmHg] | 0.0018 | $n_{a3}$ [mol] | 2.00 | $P_2$ [mmHg] | 0.0012 | $n_{a4}$ [mol] | 1.45 |
| $P_3$ [mmHg] | 0.0011 | $n_{a5}$ [mol] | 3.48 | $P_3$ [mmHg] | 0.00081 | $n_{a6}$ [mol] | 2.51 |
| $P_4$ [mmHg] | 0.00039 | $n_{a7}$ [mol] | 7.52 | $P_4$ [mmHg] | 0.00033 | $n_{a8}$ [mol] | 5.50 |
| $P_5$ [mmHg] | 0.0028 | $n_{a9}$ [mol] | 12.50 | $P_5$ [mmHg] | 0.0017 | $n_{a10}$ [mol] | 9.29 |
| $P_6$ [mmHg] | 0.0069 | $N_a$ [mol] | 0.0000037 | $P_6$ [mmHg] | 0.0049 | $N_a$ [mol] | 0.0000027 |
| $P_7$ [mmHg] | 0.013 | $M_g$ [g/mol] | 3.062 | $P_7$ [mmHg] | 0.010 | $M_g$ [g/mol] | 2.26 |
| $n_{a1}$ [mol] | 3.48 | $\rho_{CFP}$ [m$^3$/g] | 0.0021 | $n_{a1}$ [mol] | 2.55 | $\rho_{CFP}$ [m$^3$/g] | 0.0016 |
| $n_{a2}$ [mol] | 3.18 | $Ac_{s}$ [m$^2$] | 0.0049 | $n_{a2}$ [mol] | 2.323 | $Ac_{s}$ [m$^2$] | 0.0036 |

The quantitive evaluation of the uncertainty expressed as the standard deviation of the probability distribution calculated for the measurand following the guidelines established in GUM expressed in equation (1) for the surface area, where \( \frac{\partial S_{BET}}{N_A}, \frac{\partial S_{BET}}{M_N}, \frac{\partial S_{BET}}{Ac_{s}}, \frac{\partial S_{BET}}{\rho_{CFP}}, \frac{\partial S_{BET}}{n_{a,k}}, \frac{\partial S_{BET}}{P_k} \) represent coefficients of sensitivity and \( u(N_A), u(M_N), u(Ac_{s}), u(\rho_{CFP}), u(n_{a,k}), u(P_k) \) the contributions of their uncertainty. The uncertainty values of the constants present in the mathematical model were taken from the literature reports and some values of uncertainties such as the Avogadro number were taken from the NIST Chemistry WebBook [7]. The probability distributions assigned to each of the input quantities were normal distributions, except for pressure, whose uncertainty was calculated from a combination of resolution and accuracy uncertainties simulated with rectangular distributions. The uncertainty values of the moles of gas adsorbed per gram of adsorbent at different pressures was attributed a 5%.

The sensitivity coefficients were determined by numerical derivation using central finite differences, which is a numerical analysis technique that allows us to calculate an approximation of the derivative of a function at a point, using some values of the function [8]. The formula of numerical differentiation by central finite differences is presented in equation 2 [9].

\[
\left[ \frac{\partial S_{BET}}{N_A} \right] = \frac{f(N_A + h) - f(N_A - h)}{2h} \quad \text{Equation 2}
\]

The surface area and its estimated uncertainty were calculated for the two samples of TiNTs. The results, including the uncertainty budget, are presented in Tables 2 and 3.
Table 2. Uncertainty estimation Sample 1 TiNTs

| Experimental conditions: TiNTs, 90 h, reaction at 383.15 K, pH = 7.0 | $S_{BET}$ | 306.24 m$^2$/g | u(S) | 31.93 m$^2$/g |
|---|---|---|---|---|
| Input quantity | $P_1$ | $P_2$ | $P_3$ | $P_4$ | $P_5$ | $P_6$ | $n_{u3}$ | $n_{u2}$ |
| Relative contribution [%] | 1.44*10^{-8} | 1.22*10^{-8} | 4.46*10^{-8} | 5.72*10^{-8} | 3.14*10^{-8} | 1.81*10^{-8} | 6.57*10^{-10} | 4.00 | 3.82 |
| Input quantity | $n_{u3}$ | $n_{u4}$ | $n_{u5}$ | $n_{u6}$ | $n_{u7}$ | $N_4$ | $Acs$ | $M_{u4}$ | $\rho_{uTR}$ |
| Relative contribution [%] | 1.35 | 1.51 | 4.57 | 21.43 | 59.15 | 5.11*10^{-10} | 3.55 | 1.81*10^{-8} | 9.08*10^{-8} |

Table 3. Uncertainty estimation Sample 2 TiNTs

| Experimental conditions: TiNTs, 90 h, reaction at 393.15 K, pH = 7.0 | $S_{BET}$ | 226.08 m$^2$/g | u(S) | 23.57 m$^2$/g |
|---|---|---|---|---|
| Input quantity | $P_1$ | $P_2$ | $P_3$ | $P_4$ | $P_5$ | $P_6$ | $n_{u3}$ | $n_{u2}$ |
| Relative contribution [%] | 1.17*10^{-8} | 9.9*10^{-8} | 4.59*10^{-8} | 7.53*10^{-8} | 2.09*10^{-8} | 1.61*10^{-8} | 7.42*10^{-10} | 4.51 | 3.74 |
| Input quantity | $n_{u3}$ | $n_{u4}$ | $n_{u5}$ | $n_{u6}$ | $n_{u7}$ | $N_4$ | $Acs$ | $M_{u4}$ | $\rho_{uTR}$ |
| Relative contribution [%] | 1.31 | 1.46 | 4.38 | 21.05 | 59.99 | 5.11*10^{-10} | 3.55 | 1.81*10^{-8} | 9.08*10^{-8} |

The expanded uncertainty estimation is defined as half the length of a coverage interval containing a given percentage of the values reasonably attributable to the measurand with a coverage factor $k = 2$, that corresponds to a coverage level of about 95%. The expanded uncertainty of the surface area in the case studies was 31.93 m$^2$/g and 23.57 m$^2$/g, which represents about 10.43% and 10.42% of the measured surfaces. In tables 2 and 3 the relative contributions of each of the sources of uncertainty evaluated can be observed. For sample 1 and sample 2 the greatest contribution to the uncertainty was given by the moles of gas adsorbed per gram of adsorbent at different pressures. The difference in the contributions observed in each of the samples is mainly due to the fact that each pre-paved TiNT showed differences in the porosity of the material as observed in the adsorption isotherms indicated in figure 2, where perhaps this difference is associated with the temperature of TiNT preparation. The preparation and characterization of nanomaterials require advances in measurement and instrumentation capabilities to validate their properties, these measurements must be reliable and comparable at a global level. The correct identification of these sources for any measurement contributes to greater precision in decision making.

To evaluate the importance of correlation effects in the mathematical model, it was used the Monte Carlo method to estimate the uncertainty, and the results were compared with those obtained with the GUM method without correlations. Figure 3 shows the results of the comparison. It is concluded that the GUM method without correlations estimates adequately the uncertainty in the study case, so it is not necessary to include correlation terms in the GUM method in this case.
4. Conclusions

- It was possible to estimate the uncertainty of the surface area of two different types of TiNTs applying the GUM method. It is important to consider the uncertainty in all the measurement processes, because a correct uncertainty estimation is fundamental for proper decision-making and for guiding improvement actions.

- The input quantity with the higher contribution to the uncertainty of the surface area in our case was the number of moles of gas adsorbed per gram of adsorbent. These results allow to correctly orient the efforts to reduce the uncertainty of surface area measurement by adsorption-desorption isotherms. Since the amount of gas adsorbed by the sample depends on temperature, vapour pressure and the nature of the solid, the use of pressure meters with higher precision could decrease the uncertainty of the amount of gas adsorbed by mass unit of the adsorbent.

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