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A gel-derived mesoporous silica reference material for surface analysis by gas sorption
1. Textural features

N.J. Coleman*, L.L. Hench

Department of Materials, Imperial College of Science Technology and Medicine, London SW7 2BP, UK

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Abstract

Current interest in monolithic mesoporous matrices requiring carefully tailored architectures has dictated the requirement for a new generation of standard materials for textural analysis. Accordingly, the textural characteristics of a mesoporous gel-derived silica monolith have been investigated by nitrogen sorption. Specific surface area (165.5 ± 1.5 m^2 g^{-1}), specific pore volume (0.986 ± 0.020 cm^3 g^{-1}), average pore size (119.2 ± 2.7 Å) and distribution are reported. The properties of the mesoporous silica were found to compare favourably with those of commercially available certified reference materials for BET surface area and pore size analysis. The primary advantage of the gel-silica monolith in this application is the elimination of errors associated with powder sampling. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Gel-derived mesoporous silica; Reference materials for surface analysis

1. Introduction

Many new types of materials with mesoporous architectures are currently being developed, as indicated in recent reviews [1–11]. These developments are relevant to a number of diverse fields, such as catalysis [1,12,13], molecularly tailored surface reactive solids [14], biomedical materials [3], and hybrid optics [4]. Thus, textural characterisation of mesoporous materials has become of increasing importance.

Gas sorption (in particular, nitrogen sorption) is a well established method for the characterisation of textural properties of solid surfaces. The technique may be used to determine the specific surface area of disperse or porous solids. Specific pore volume, average and modal pore size and distribution may also be estimated. A number of texts are available in which the theory, principles, instrumentation and applications of gas sorption are discussed [15–17].

To ensure correct instrument performance and data evaluation, apparatus should be monitored periodically using a surface area reference material. Currently, all standard reference materials (hereafter SRMs) for surface area analysis by nitrogen sorption which are commercially available in the UK and in Europe, via the European Commission's Institute for Reference Materials and Measurements (IRMM), are in powder form [18,19]. The largest supplier of SRMs in the UK, Laboratory of the Government Chemist (LGC), markets a comprehensive range of SRMs from IRMM, Bundesanstalt für Materialforschung und -prüfung (BAM) and the National Institute of Standards and Technology (NIST), as well as its own certified materials. Standard reference materials of surface areas ranging from 0.0686 to 258.0 m^2 g^{-1} are available.

The BAM is the only establishment which produces SRMs for pore size analysis. Both are mesoporous alumina powders, designated, CRM BAM-PM-103 and CRM BAM-PM-104. The textural characteristics of the powders are listed in Table 1 [20]. Each tabulated property listed in Table 1 is the arithmetic mean of measurements made in at least 22 laboratories. The uncertainty is expressed as the standard deviation of this mean divided by the square root of the number of participating laboratories. The mean pore radius, r, is estimated using the following relationship (which assumes cylindrically shaped pores):

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* Corresponding author. Tel.: +44-(0)171-589-5111; fax: +44-(0)171-594-6809.

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Table 1
The textural characteristics of BAM mesoporous alumina reference materials for pore size analysis

	Specific surface area (m^2 g^{-1})	Specific pore volume (cm^3 g^{-1})	Mean pore radius (Å)
Alumina			
CRM BAM-PM-103			
Mean value	156.0	0.250	31.8
Standard deviation(s)	7.2	0.008	0.8
% Standard deviation	4.6	3.2	2.5
Uncertainty	±1.3	±0.002	±0.2
Alumina			
CRM BAM-PM-104			
Mean value	79.8	0.210	53.1
Standard deviation(s)	2.0	0.009	2.4
% Standard deviation	2.5	4.3	4.5
Uncertainty	±0.4	±0.002	±0.5

$$r = \frac{2V_p}{S_{\mathrm{BET}}} \tag{1}$$

where V_p is the specific pore volume and S_{BET} is the surface area calculated using the BET method [21].

A number of disadvantages are associated with the use of powders as reference materials for surface analysis. Powder sampling methods introduce errors which become successively more significant. Standard deviations for sampling errors of up to 6.8% have been reported [22]. Not only is powder handling inconvenient, but also, sample preparation of powders for surface analysis is comparatively time-consuming. A low rate of evacuation must be applied to powder samples during outgassing to prevent disturbance and migration of the powder. Higher, more efficient, rates of evacuation can be used during sample preparation and analysis of monolithic materials. Hence, a stable, durable monolith having a controlled surface texture and geometry would be ideal as a standard reference material for surface area and pore size analysis. A monolithic silica standard reference material is especially desirable due to the recent interest in structured mesoporous silicate materials [1–14].

Since the early 1980s research into the fundamental science of alkoxide-derived oxides has been growing [23–27]. Greater understanding and control of sol–gel processing has enabled the production of novel ceramic components for a variety of applications, which include optical and chemical sensors, waveguides and biomaterials [28–32].

Higher product purity and homogeneity and lower processing temperatures, compared with those of traditional glass melting or ceramic powder methods, have been the primary stimuli for the increasing interest in sol–gel science [33]. Another advantage of sol–gel processing is the ability to modify the textural properties of materials during the seven-stage processing route. The versatility of the process allows control of metric features, such as specific surface area, volume fraction of porosity, pore size and distribution and geometry.

Following thermal stabilisation between 700 and 1000°C the surface of porous gel-silica is composed almost entirely of siloxane bonds which can withstand atmospheric exposure indefinitely. Some densification occurs during this treatment although a large volume fraction of stable, interconnected porosity of exceptionally narrow pore size distribution, remains [28,34,35].

It is proposed that this method of processing can be used to design monolithic ceramic oxides which are suitable for use as standard reference materials for surface area and pore size analysis. The textural characteristics of one such monolithic gel-derived silica material are reported here.

A number of IUPAC programmes on the standardisation of procedures for the determination and reporting of textural characteristics of porous and non-porous materials have been conducted [36,37]. The International Standard, ISO 9277:1995(E), 'Determination of the specific surface area of solids by gas adsorption using the BET method', is based on the 1984 IUPAC Recommendations. Nitrogen sorption data has been collected, analysed and reported in compliance with this International Standard.

2. Experimental

2.1. Sample preparation

Cylindrical gel–silica monoliths (height 2.5 mm×diameter 5.6 mm) were prepared by the acid catalysed hydrolysis and condensation of an alkoxysilane precursor, following procedures reviewed in Ref. [4]. The specimens were stabilised at 900°C. Samples were stored in polyethylene bags in a screw-top polypropylene jar over self-indicating silica gel and analysed at intervals over a 9 month period.

2.2. Textural characterisation

The textural characterisation was performed on a six port Quantachrome AS6 Autosorb and two single port Quantachrome AS1 Autosorb gas sorption systems. The instruments determined isotherms volumetrically by a discontinuous static method at 77.4 K [38]. The adsorptive gas was nitrogen, N_2, of 99.999% purity. The cross sectional area of adsorbed nitrogen molecules was taken to be 0.162 nm^2 for the purposes of specific surface area calculations [39].

Prior to nitrogen sorption, all samples were heated under vacuum pressure lower than 1 Pa at 100°C for 12 h to remove physically adsorbed material from their surfaces. The specific surface areas were estimated in relation to the masses of the degassed samples.

Four instrument operators collected duplicate N_2 isotherms on a total of 17 gel–silica monoliths selected at random from a batch of 1000. Each silica monolith was analysed individually. Each isotherm comprised a minimum of 20 adsorption and 20 desorption points measured at equilibrium. At least four adsorption points in the relative pressure range $0.05 < P/P_o < 0.30$ (where P_o is the saturated vapour pressure) were used in the calculation of the BET surface area in each case, as stipulated in ISO 9277:1995. It was ensured that the slope and intercept of the BET plots were positive and that the product moment correlation coefficients were not less than 0.99991. Two isotherms were collected for each monolith to ensure that the data was representative. Data from the second isotherms has been used in the evaluation of the textural parameters which are reported here. All sources of error; instrument accuracy, sample, instrument and operator variation, are combined and reflected in the statistical treatment of the data.

2.3. Treatment of data

The most widely employed model for the evaluation of specific surface area is the BET method which is based upon the measurement of quantities of gas physisorbed onto a surface at equilibrium pressure [21]. This method yields reliable results for isotherms of type II and IV (according to Brunauer and IUPAC classifications) [36,38,40].

The monolayer capacity (the amount of adsorbate required for surface coverage of a complete monolayer of molecules) of a specimen, n_m, is estimated using the BET equation:

$$\frac{\frac{P}{P_o}}{n\left[1-\left(\frac{P}{P_o}\right)\right]}=\frac{1}{n_m C}+\frac{C-1}{n_m C}\left(\frac{P}{P_o}\right) \quad (2)$$

where n is the amount of gas adsorbed, P is pressure, P_o is saturation pressure and C is the BET constant. $(P/P_o)/n[1-(P/P_o)]$ plotted against (P/P_o) should give a rectilinear plot of the form $y = a + bx$ where a is the intercept and b is the gradient. The monolayer capacity is then,

$$n_m = \frac{1}{a+b} \quad (3)$$

and the BET constant is given by:

$$C = \frac{b}{a} + 1 \quad (4)$$

The surface area, S_{BET}, of the specimens is then estimated, thus:

$$S_{\mathrm{BET}} = n_m L a_m \quad (5)$$

where L is Avogadro's constant and a_m is the molecular cross-sectional area occupied by an adsorbed molecule in a complete monolayer.

Estimates of specific pore volume were obtained from the amount of nitrogen taken up by the samples in the range $0.994 < P/P_o < 0.999$. Pore size distributions were calculated from desorption data by the BJH method [41]. The mean pore radius was calculated according to Eq. (1).

The standard deviations of the means of the specific surface area, specific pore volume and average pore radius were calculated. The standard deviation of the average pore radius was estimated by considering the multiplicative propagation of random errors [42]. One measure of uncertainty was evaluated by dividing the standard deviation by the square root of the number of samples tested. This allowed a comparison between the uncertainties associated with the BAM certified reference materials, CRM BAM-PM-103 and CRM BAM-PM-104, and those of the gel-silica monolith investigated here. The 95% confidence limits were also estimated [42]. It was assumed that the sample population conformed to a Gaussian distribution [42].

3. Results

The isotherm shown in Fig. 1 is representative of those collected for all of the gel-silica monoliths. The isotherm is of type IV indicating that the samples are mesoporous (i.e. they possess pore diameters in the range 20 to 500 Å) [36].

Hysteresis in the multilayer region of the isotherm, denoted by the deviation in pathway of the adsorption and desorption data, is associated with capillary condensation in the mesopore structure. The hysteresis loop is of type H1 (formerly type A) which indicates the presence of cylindrical pores of narrow pore distribution [36,43]. The loop closes and the isotherm forms a plateau, from $P/P_o \sim 0.97$, before a relative pressure approaching unity is reached. An advantage of this behaviour is that it allows the measurement of total pore volume at a relative pressure which is considerably lower than the saturated equilibrium vapour pressure, P_o, thus reducing the risk of condensation during data acquisition at the top of the isotherm.

A representative BET plot is shown in Fig. 2. The intercept is close to the origin, typifying nitrogen adsorption on oxides, which is indicative of an adequately large C value [15]. The C value denotes the degree of interaction between the adsorptive gas and the

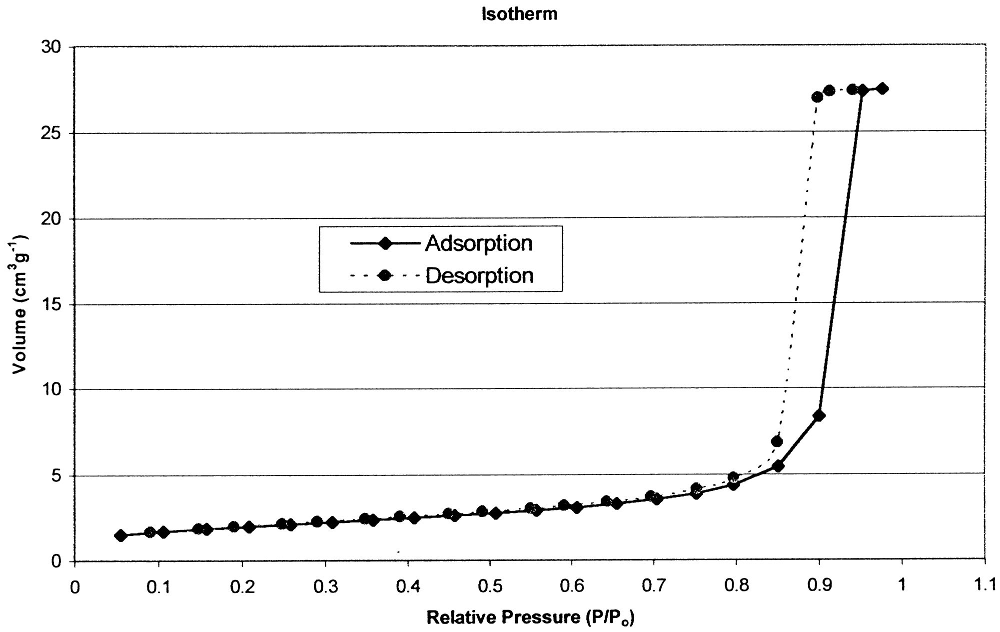

Fig. 1. Adsorption–desorption isotherm of nitrogen at 77.4 K on mesoporous gel–silica.

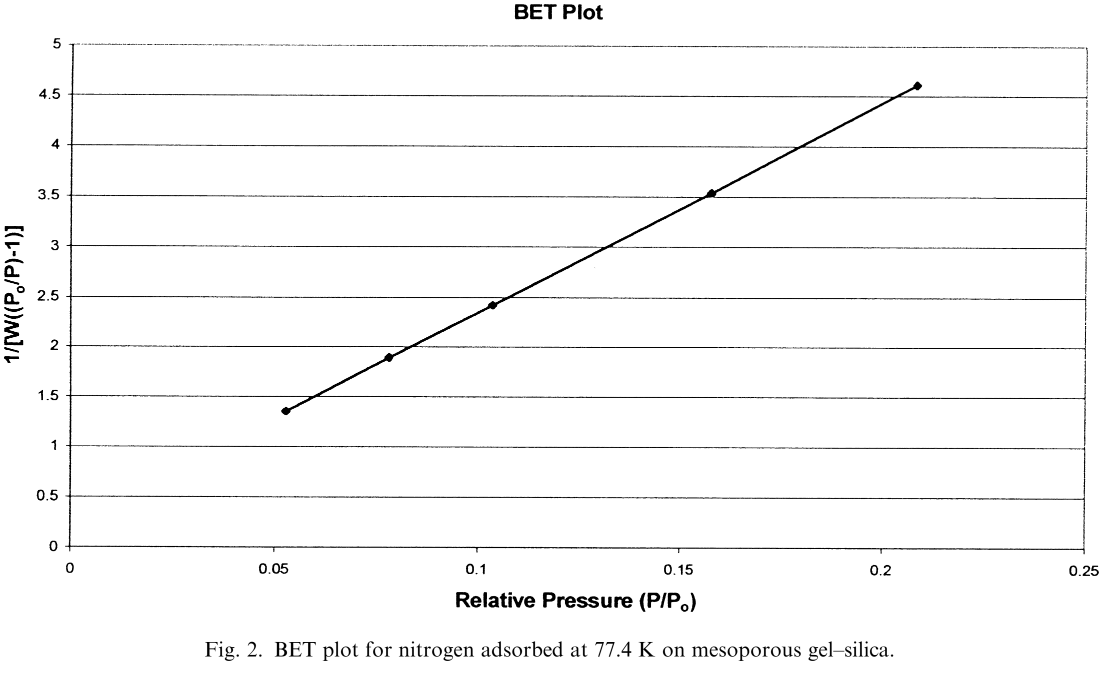

Fig. 2. BET plot for nitrogen adsorbed at 77.4 K on mesoporous gel–silica.

solid surface; large C values are associated with strong interactions. The mean C value for the adsorption of nitrogen on the gel-silica samples is 105. The BET equation indicates the amount of adsorbate required to form a single molecular layer although no such uniform monolayer actually exists in the case of real physical adsorption. The C value may be used to estimate the fraction of the surface which is unoccupied when 'sufficient' adsorption has occurred. In this case it is 0.091, i.e. the surface is essentially covered with a monolayer and the BET theory is applicable [44].

The textural parameters of the monolithic gel-silica are presented in Table 2. A difference in specific surface area, between the first and second measurements, of less than 3% was obtained, indicating that the results are highly reproducible. The mean specific surface area of the mesoporous gel-derived silica monolith is estimated at 165.5 ± 1.5 m^2 g^{-1}. The mass of each monolith is

Table 2
The textural characteristics of gel-derived mesoporous silica

	Specific surface area (m^2 g^{-1})	Specific pore volume (cm^3 g^{-1})	Mean pore radius (Å)
Gel–silica monolith			
Mean value	165.5	0.986	119.2
Standard deviation(s)	3.0	0.039	5.2
% Standard deviation	1.8	3.9	4.4
Uncertainty	±0.7	±0.009	±1.3
95% Confidence limits	±1.5	±0.020	±2.7

approximately 0.044 g and results in a total nitrogen uptake of around 650 cm^3 g^{-1} (corrected to STP).

The pore size and volume distributions, according to the BJH model, are depicted in Figs. 3 and 4, respectively. The range of pore sizes compares favourably with those of other materials reported in recent literature as potential surface area and pore size analysis reference materials [45]. The modal pore diameter, as indicated in Fig. 3, is approximately 174 Å. Hence, the modal pore radius, ~87 Å, is notably smaller than the mean pore radius, 119.2 Å. The difference between the two quantities arises from a combination of factors; deviation from perfect cylindrical geometry, the volume associated with the junctions of the pores, and the existence of a small number of large pores (as shown in Figs. 3 and 4). *t*-Method analysis (in which a monolayer of nitrogen molecules was taken to be 3.54 Å) indicated the absence of micropores [46].

4. Discussion

The textural data and statistical analysis of the BAM certified reference materials (Table 1) reflect inter-laboratory variation (from between 22 and 30 different establishments). The statistical treatment performed here on the textural data for mesoporous gel-silica (Table 2) reflects the variation of four operators and eight instrument ports for a sample population of 17. Inter-laboratory variation would be expected to increase the standard deviations, *s*, of each mean textural parameter of the BAM SRMs relative to those of the mesoporous gel-silica. However, the larger sample population of the former would tend to reduce this statistic. Accordingly, the two sets of data presented in Tables 1 and 2 can be compared with some degree of confidence. Standard deviations have been expressed as percentages of the means (relative standard deviations) of each of the textural parameters to facilitate comparison.

The relative standard deviations (hereafter RSDs) of the mean specific surface area, specific pore volume and mean pore radius for BAM SRMs and mesoporous gel-silica are listed in Tables 1 and 2, respectively. Comparison of the RSDs indicates that the degree of precision obtained in the evaluation of the textural

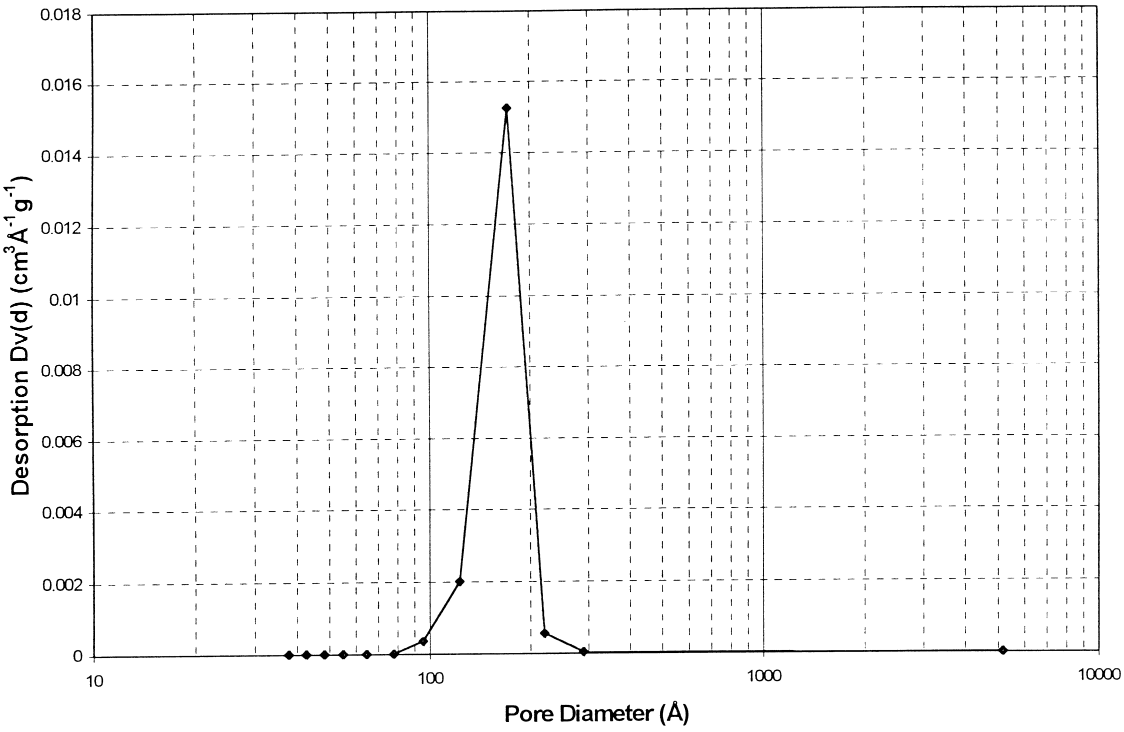

Fig. 3. Pore size distribution of mesoporous gel–silica, calculated by the BJH method from the desorption branch of the nitrogen isotherm at 77.4 K.

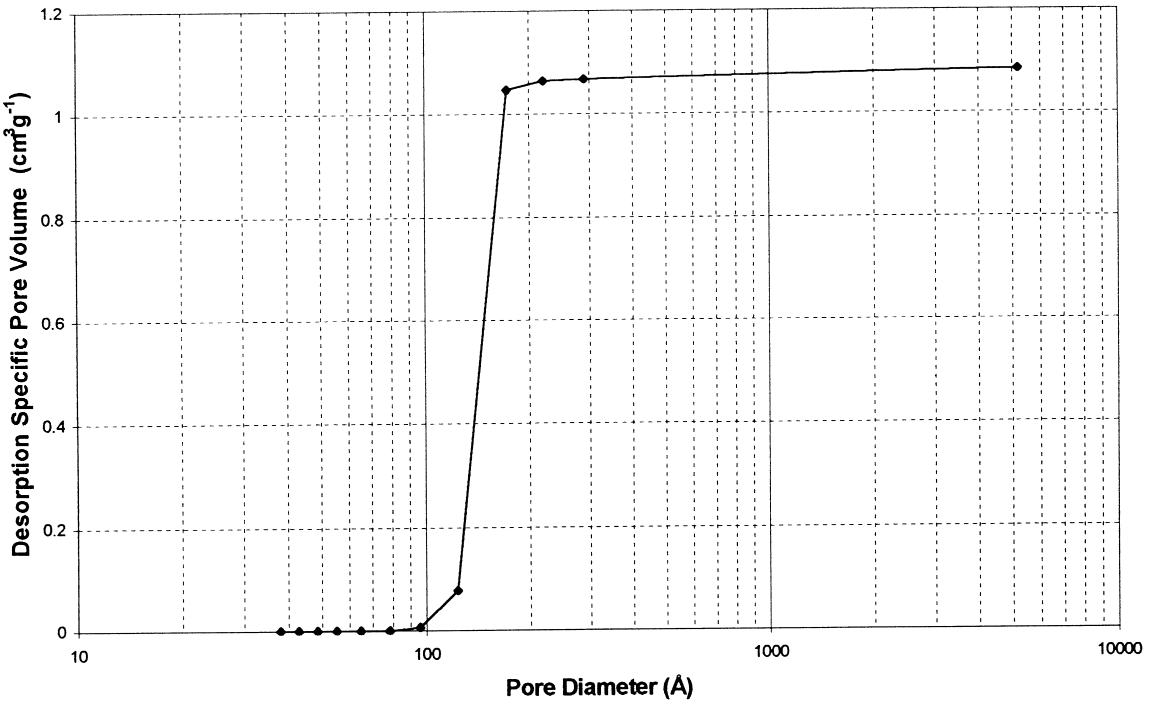

Fig. 4. Cumulative pore volume of mesoporous gel–silica, calculated from the desorption branch of the nitrogen isotherm at 77.4 K.

parameters from nitrogen sorption measurements is very similar for all three materials.

The RSD of the mean specific surface area of the gel-silica, 1.8%, is marginally lower than those of the BAM SRMs, 2.5 and 4.6%. This difference is not considered to be significant owing to the difference in methods of data collection for the three materials (as discussed above). The RSDs of the specific total pore volume and mean pore radius of the gel-silica are intermediate between those reported for the BAM SRMs.

For a normally distributed sample population approximately 68% of the population lies within ± 1s of the mean and approximately 95 and 99.7% of values lie within ± 2s and ± 3s of the mean, respectively. Hence, the statistics in Table 2 indicate that S_{BET} of approximately 680 of the batch of 1000 silica monoliths will be in the range $162.5 < S_{\mathrm{BET}} < 168.5$ m^2 g^{-1}. Accordingly, 68% of the samples will possess specific pore volumes, V_p, in the range $0.947 < V_p < 1.025$ cm^3 g^{-1} and mean pore radii, r, of $114.0 < r < 124.4$ Å.

A confidence interval is used to define a range within which it may be reasonably assumed that a true value lies. The confidence limits are the extreme values of this range. The 95% confidence limits reported in Table 2 for the measurement of S_{BET}, for example, indicate that there is a 95% probability that the mean value of S_{BET} for the entire batch of samples would lie in the range 165.5 ± 1.5 m^2 g^{-1}. Estimates of uncertainties and confidence limits, as tabulated in Tables 1 and 2, do not indicate that the mean value of a textural parameter of an individual standard material should be expected fall within those limits.

During the past few years significant progress has been made in the control of the compositions and morphologies of mesoporous materials [47]. The full potential of the new generation of highly ordered mesoporous materials currently being explored is yet to be realised. The recent research initiatives in the synthesis of mesoporous silica matrices include materials for large-molecule catalysis [13,47,48], sensors [47], drug delivery [49], separation processes [50], biomedical ceramics [3,51], and hybrid optics [4]. The performance of each type of material cited above is strongly dependent on its textural features, especially pore volume, pore size and pore size distribution. This current interest in monolithic mesoporous matrices requiring carefully tailored architectures has dictated a requirement for a new generation of standard materials for textural analysis. The textural properties of the mesoporous gel-silica monolith reported here indicate that such materials would satisfy this requirement. The durability and stability of the monolithic gel-derived silica are documented elsewhere [52].

5. Conclusions

The findings of an investigation into the textural features — specific surface area (165.5 ± 1.5 m^2 g^{-1}), specific pore volume (0.986 ± 0.020 cm^3 g^{-1}) and mean pore diameter (119.2 ± 2.7 Å) — of a gel-derived silica monolith are presented here. Statistical analysis indicates that, on the basis of these textural parameters, this material compares favourably with other commercially available standard reference materials for surface area and pore size analysis. The advantages of the gel-silica in this application are that, since it is monolithic, it is more convenient to use and errors associated with powder sampling are eliminated.

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