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A gel-derived mesoporous silica reference material for surface analysis by gas sorption 2. Durability and stability

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Abstract

The characterisation of novel mesoporous films, spheres, fibres and monoliths requires a new generation of standard materials for textural analysis. The textural characteristics of a mesoporous gel-derived silica monolith, investigated by nitrogen sorption are: specific surface area (165.5 ± 1.5 m^2 g^{-1}), specific pore volume (0.986 ± 0.020 cm^3 g^{-1}) and average pore size (119.2 ± 2.7 Å). The effects of storage and usage on the textural properties of the gel-silica have been monitored for up to 12 months by nitrogen sorption. Non-parametric statistical analysis indicated that no significant changes in textural features had occurred following either a year of storage or repeated usage.

1. Introduction

Many novel materials with mesoporous architectures are currently being developed, as indicated in recent reviews [1–14]. Research initiatives in the synthesis of mesoporous silica matrices include materials for large-molecule catalysis [13,15,16], sensors [15], drug delivery [17], separation processes [18], biomedical ceramics [4,19], and hybrid optics [5]. 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 interest in monolithic mesoporous matrices with carefully tailored architectures has stimulated the need for a new generation of monolithic standard materials for textural analysis which are environmentally stable and can be used repeatedly.

Gas sorption (in particular, nitrogen sorption) is an 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 [20–22].

To ensure correct instrument performance and data evaluation, apparatus require periodic monitoring using a 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 [23,24].

The Bundesanstalt für Materialforschung und -prüfung (BAM), Germany, is the only establishment which produces SRMs for pore size analysis [25]. Both are mesoporous alumina powders, designated CRM BAM-PM-103 and CRM BAM-PM-104.

A number of disadvantages are associated with the use of powders as reference materials for surface analysis, as recently discussed by the authors [26]. In a previous paper the authors reported the textural features of a gel-derived mesoporous silica monolith which are summarised in Table 1 [26]. Statistical analysis indicated that, on the basis of textural parameters, the silica monolith compares favourably with the mesoporous alumina powders, CRM BAM-PM-103 and CRM BAM-PM-104 which are commercially available from BAM. The advantages of the gel-silica material in this application are that, since it is monolithic, it is more convenient to use and errors associated with powder sampling are eliminated [26,27].

Durability and stability are essential requirements of a monolithic standard reference material which is intended to be stored and used repeatedly. Durability,

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Table.1
Textural properties of the mesoporous gel-silica monolith

	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

in this context, refers to the performance of the monolith as a function of repeated usage. The production of a nitrogen sorption isotherm necessitates an outgassing regime at elevated temperature (in this case, 100°C) and the collection of data at −196°C. One prerequisite of a monolithic standard reference material is that its surface characteristics remain unchanged when it is subjected to repeated thermal treatment of this nature. The durability of the gel-silica monolith has been evaluated by measuring the specific surface area and specific pore volume, by nitrogen sorption, as functions of repeated usage.

The term 'stability' is used to denote the textural features of the material as a function of (storage) time. The stability of the mesoporous gel-silica has been assessed by monitoring the specific surface area and specific pore volume, by nitrogen sorption, at monthly intervals over the period of 1 year. The Wald–Wolfowitz statistical method, a test for trends and tendencies, has been employed in the examination of the data [28].

2. Experimental

2.1. Sample preparation

A batch of 1000 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.

2.2. Textural characterisation

The textural characterisation was performed on a six port Quantachrome AS6 Autosorb gas sorption system. The instrument determined isotherms volumetrically by a discontinuous static method at 77.4 K [29]. 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 [30].

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.

Each silica monolith was analysed individually. Each isotherm comprised a minimum of 20 adsorption and 20 desorption points measured at equilibrium. The most widely employed model for the evaluation of specific

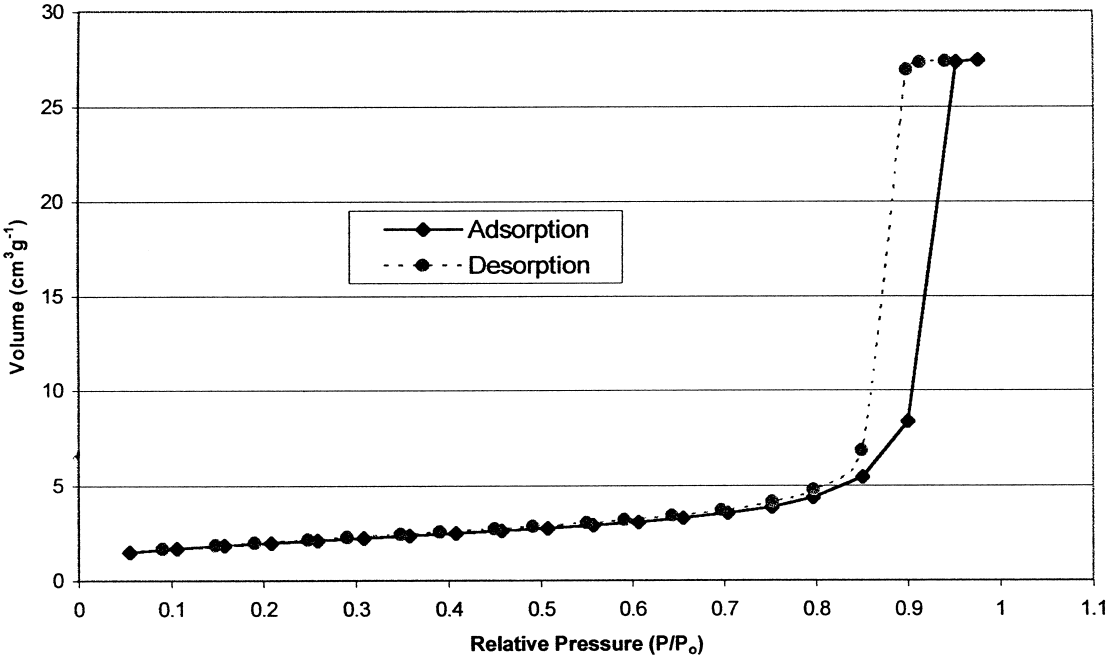

Fig. 1. Adsorption–desorption isotherm of nitrogen at 77.4 K on mesopourous gel-silica.

surface area is the BET method which is based upon the measurement of quantities of gas physisorbed onto a surface at equilibrium pressure [31]. 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 [29]. 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 0.9999.

Estimates of specific pore volume were obtained from the amount of nitrogen taken up by the samples in the range $0.994 < P/P_o < 0.999$.

2.2.1. Durability investigation

Five gel-silica monoliths, selected at random from the batch of 1000, were outgassed and analysed by nitrogen sorption, as described in the previous section. The procedure was then repeated 10 times. The mean values of BET specific surface area and total pore volume for each analysis were recorded.

2.2.2. Stability investigation

Four gel-silica monoliths, which had been stored in polyethylene bags in a screw-top polypropylene jar over self-indicating silica gel, were selected at random from the batch of 1000 each month for a period of 1 year. The monoliths were subjected to the outgassing and nitrogen sorption analysis procedures outlined in Section 2.2. Two isotherms were collected for each monolith to ensure that the data were representative.

Data from the second isotherms have been used in the evaluation of the textural parameters which are reported here. 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.

2.3. Treatment of data

2.3.1. Comparison of the means of two sample populations

In this method the null hypothesis, that there is no significant difference between two mean values, is tested [28]. A combined estimate of the standard deviation is calculated from the two individual standard deviations s_1 and s_2, thus:

$$s^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)n_2^2}{n_1 + n_2 - 2} \quad (1)$$

Table 2
Durability data: specific surface area, S_{BET}, as a function of usage

Usage (number isotherms collected)	Specific surface area S_{BET} ($m^2 g^{-1}$)	Standard deviation of S_{BET} ($m^2 g^{-1}$)	Residual ($m^2 g^{-1}$)
1	164.6	2.7	1.65
2	162.9	2.1	−0.05
3	162.9	2.9	−0.05
4	164.2	2.8	1.25
5	163.0	1.8	0.05
6	162.3	3.3	−0.65
7	162.9	2.3	−0.05
8	161.7	2.8	−1.25
9	163.4	2.5	0.45
10	164.6	3.1	1.65
Median	162.95		

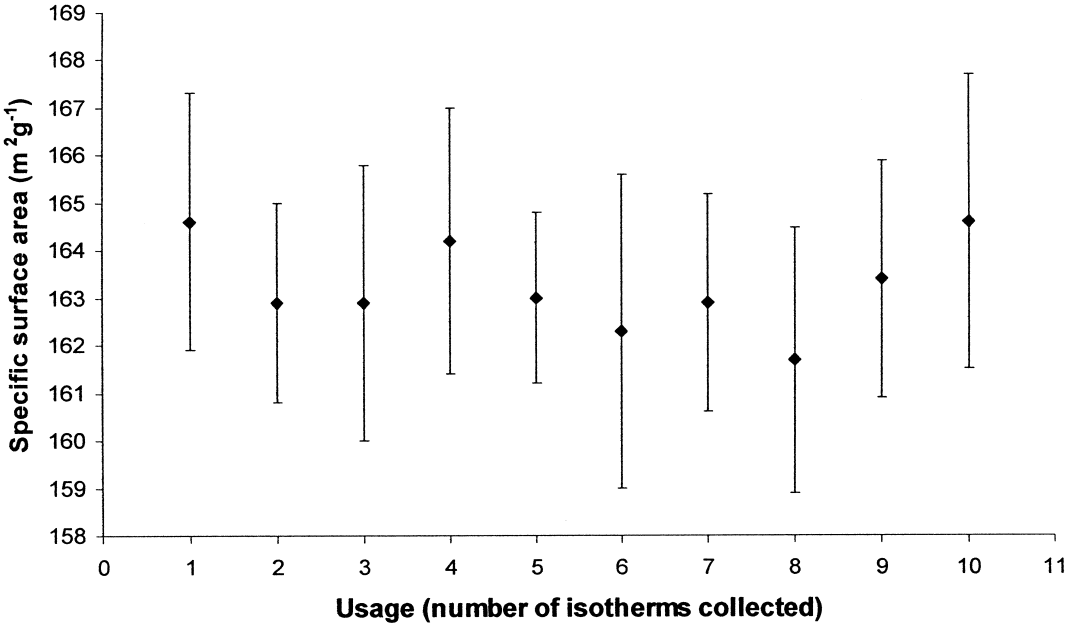

Fig. 2. Specific surface area, S_{BET}, as a function of usage.

The statistic, t, is then given by:

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \quad (2)$$

where t has $n_1 + n_2 - 2$ degrees of freedom.

If the calculated value of the modulus of t is less than the critical value (tabulated in t-distribution tables) the difference between the two means is not significant and the null hypothesis is retained. This method was used to compare the textural parameters listed in Table 1 with the data reported herein (both having been derived from the same batch of samples). The textural parameters listed in Table 1 are the means of 17 measurements. All data reported here were not found to be statistically different from those listed in Table 1 at the 2% significance level.

2.3.2. The Wald–Wolfowitz method

Non-parametric (or distribution-free) statistical methods are those which make no assumption about the shape of the distribution from which data are taken. The mean is an adequate measure of central tendency for symmetrically (normally) distributed data. In non-parametric statistics the median is a more appropriate measure. A median is calculated by arranging n observations is ascending order. The median value is the value of the $1/2(n+1)$th observation if n is odd: and the arithmetic mean of the $1/2n$th and $(1/2n+1)$th observations if n is even.

The objective of the investigation reported herein is to assess whether the textural parameters of the gel-silica monoliths change as functions of storage and usage. The median is determined for each set of data. The median value is then subtracted from each experimental value in turn and the sign of the difference between the two (the residual) is recorded. Zero residuals are ignored. A random sequence of signs indicates that there is no trend in the data.

A sequence of positive or negative signs is referred to as a run. The Wald–Wolfowitz method tests whether the number of runs is sufficient for the null hypothesis of a random distribution to be rejected [28]. The number of runs generated by the experimental data is compared with tabulated values which refer to the 5% significance level. Using this level of significance there is, on average, a 5% probability that a null hypothesis will be rejected when it is, in fact, true.

Table 3
Durability data: specific pore volume, V_p, as a function of usage

Usage (number of isotherms collected)	Specific pore volume V_P ($cm^3\ g^{-1}$)	Standard deviation of V_P ($cm^3\ g^{-1}$)	Residual ($cm^3\ g^{-1}$)
1	0.9988	0.030	0.0014
2	0.9972	0.031	−0.0002
3	1.0030	0.031	0.0056
4	0.9966	0.030	−0.0008
5	0.9994	0.029	0.0020
6	0.9980	0.032	0.0006
7	0.9973	0.030	−0.0001
8	0.9947	0.031	−0.0027
9	0.9974	0.031	0
10	0.9964	0.031	−0.0010
Median	0.9974		

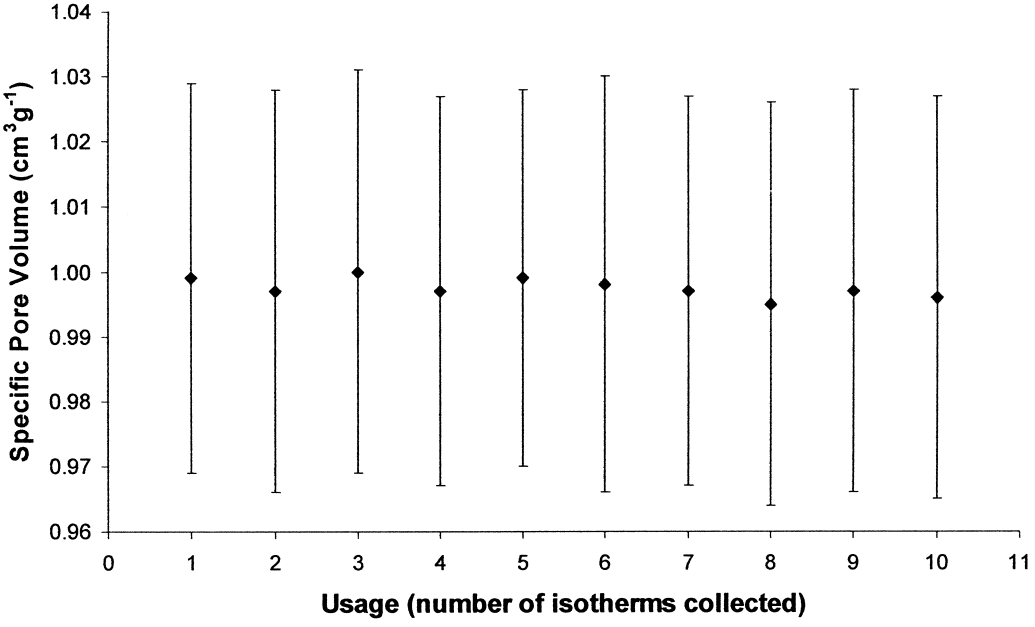

Fig. 3. Specific pore volume, V_p, as a function of usage.

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 20–500 Å) [32]. *t*-Method analysis (in which a monolayer of nitrogen molecules was taken to be 3.54 Å) indicated the absence of micropores [33].

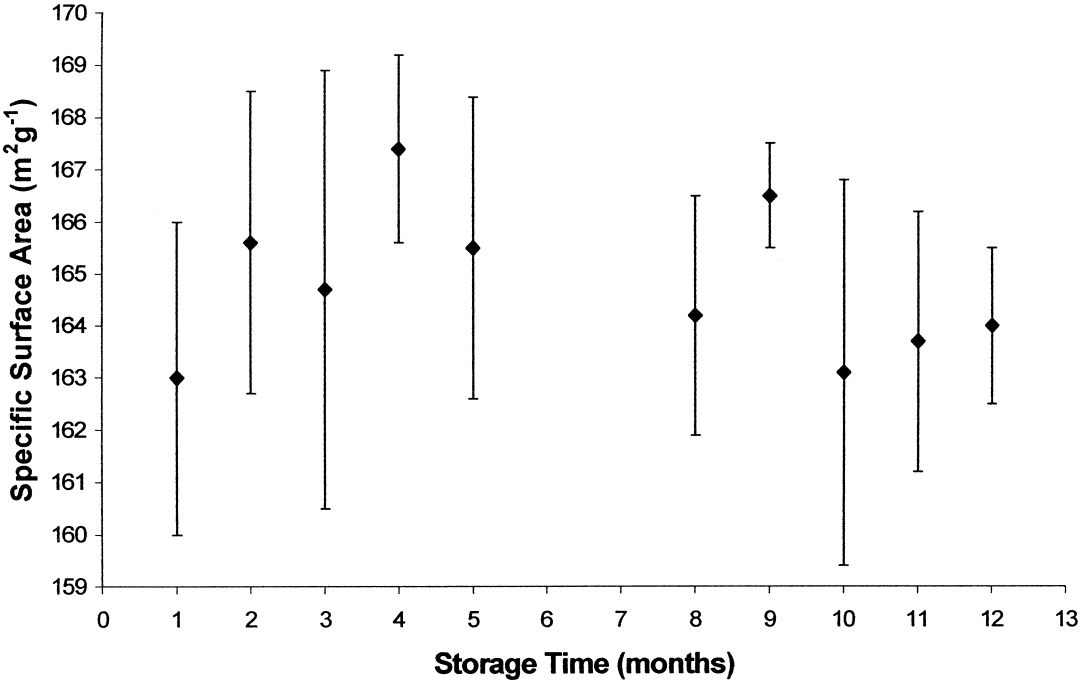

Fig. 4. Specific surface area, S_{BET}, as a function of storage time.

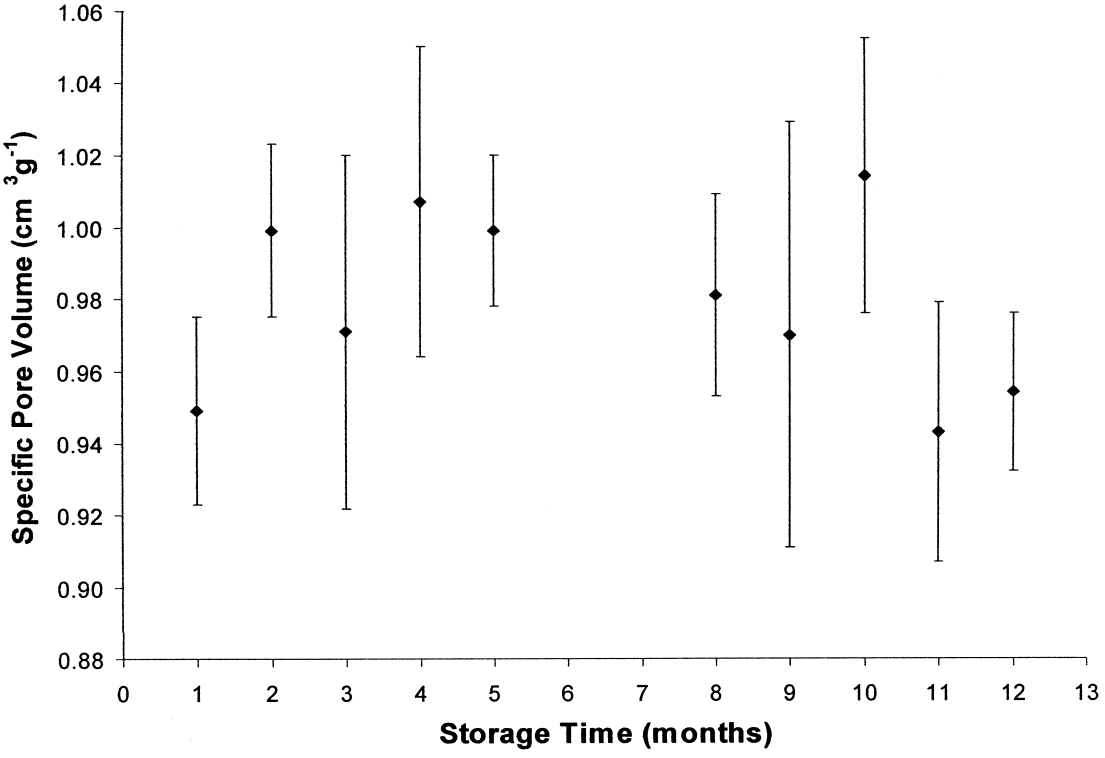

Fig. 5. Specific pore volume, V_p, as a function of storage time.

The specific surface area of the monolithic gel-silica as a function of usage is presented in Fig. 2 and Table 2. Specific pore volume as a function of usage is depicted in Fig. 3 and listed in Table 3. The textural parameters of the gel-silica as functions of storage time are presented in Figs. 4 and 5, and Tables 4 and 5. The error bars in Figs. 2–5 represent one standard deviation of each mean value which has been plotted.

The final column in Tables 2–5, entitled 'Residual', lists the difference between each experimental value and the median (as discussed in Section 2.3.2). The number of positive and negative residuals (N and M, respectively) for each set of data is presented in Table 6, which also lists the number of runs, R. The null hypothesis, of a random distribution, is retained in each case as the number of runs lies outside the necessary boundary conditions for the rejection of the null hypothesis.

4. Discussion

Durability and stability are essential requirements of a monolithic reference material which is to be used repeatedly and stored for long periods. The BET specific surface area and specific pore volume of the mesoporous gel-silica monolith as functions of usage and storage time are depicted in Figs. 2–5. By visual inspection, there is no apparent trend in textural properties as functions of either usage or storage time.

The Wald–Wolfowitz method, which tests the null hypothesis of a random distribution of data by analysing the signs of the residuals of the median, was employed to test for trends in the textural parameters of the gel-silica as functions of usage and storage (Section 2.3.2. and Table 6). In each case the null hypothesis was retained at the 5% significance level. Retention of the null hypothesis indicates that there is no significant change in either BET specific surface area or specific pore volume as functions of usage and storage time (for the selected analysis and storage regimes). Thus, the mesoporous gel-silica has been shown to be sufficiently durable to give reproducible surface area and pore volume data from at least ten consecutive analyses. The stability of the silica monolith is such that storage over self-indicating silica desiccant at room temperature for up to 1 year has had no significant effect on its texture.

Since the early 1980s research into the fundamental science of alkoxide-derived oxides has been growing [34–38]. 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 [35,39–41]. One 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, geometry and distribution.

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

Table 4
Stability data; specific surface area, S_{BET}, as a function of storage time

Storage time (months)	Specific surface area S_{BET} ($m^2\ g^{-1}$)	Standard deviation of S_{BET} ($m^2\ g^{-1}$)	Residual ($m^2\ g^{-1}$)
1	163.0	3.0	−1.45
2	165.6	2.9	1.15
3	164.7	4.2	0.25
4	167.4	1.8	2.95
5	165.6	2.9	1.15
8	164.2	2.3	−0.25
9	166.5	1.0	2.05
10	163.1	3.7	−1.35
11	163.7	2.5	−0.75
12	164.0	1.5	−0.45
Median	164.45		

Table 5
Stability data: specific pore volume, V_p, as a function of storage time

Storage time (months)	Specific pore volume V_p ($cm^3\ g^{-1}$)	Standard deviation of V_p ($cm^3\ g^{-1}$)	Residual ($cm^3\ g^{-1}$)
1	0.9485	0.026	−0.0270
2	0.9985	0.024	0.0230
3	0.9714	0.049	−0.0041
4	1.0073	0.043	0.0318
5	0.9988	0.021	0.0233
8	0.9796	0.028	0.0041
9	0.9696	0.059	−0.0059
10	1.0141	0.038	0.0386
11	0.9428	0.036	−0.0327
12	0.9542	0.022	−0.0213
Median	0.9755		

Table 6
The number of + signs, N, number of − signs, M, number of runs R, and the conditions for the rejection of the null hypothesis for the durability and stability data

Data series	No. of + signs, N	No. of − signs, M	No. of runs, R	Conditions for rejection of null hypothesis
S_{BET} durability data (from Table 2)	5	5	5	$R<3$ or $R>9$
V_p durability data (from Table 3)	4	5	7	$R<3$ or $R>8$
S_{BET} stability data (from Table 4)	5	5	5	$R<3$ or $R>9$
V_p stability data (from Table 5)	5	5	7	$R<3$ or $R>9$

pore size distribution, remains [42–44]. The resulting silica network is sufficiently durable to resist deformation and cracking when repeatedly exposed to the aggressive temperature and pressure regimes which are associated with textural characterisation by nitrogen sorption.

It is proposed that this method of processing can be used to design stable, durable, monolithic ceramic oxides which are suitable for use as standard reference materials for surface area and pore size analysis.

5. Conclusions

The durability and stability of gel-derived silica monoliths, whose performance as reference materials for nitrogen sorption compares well with those of other commercially available standard reference materials for surface area and pore size analysis, have been evaluated [26]. Non-parametric statistical analysis indicates that no significant changes in either BET specific surface area or specific pore volume occurred following either a year of storage or repeated exposure to the thermal and pressure cycles associated with nitrogen sorption analysis.

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