

TITRIMETRIC AND GRAVIMETRIC DETERMINATION OF THE SPECIFIC PORE VOLUME OF MICROPARTICULATE SILICA GELS

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The titrimetric and gravimetric methods of determination of the specific pore volume were studied for unmodified and modified chromatographic silica gels of mean particle size above $5\ \mu\text{m}$. The apparatus and titrimetric procedure suggested elsewhere were adapted so that the relative standard deviation of measurement did not exceed 2%. Water, n-octane, and methanol were used as titrants, and methanol was found to suit best from the point of view of accuracy and rapidity of analysis and versatility of use. This solvent is also suitable for the gravimetric measurements, which can be carried out without thermostating and at barometric pressure. The titrimetric procedure is less time consuming than the gravimetric procedure which, on the other hand, is less tedious and less instrumentation-demanding.

Among the basic parameters of porous solid substances is their specific pore volume V_p . From the published methods for its determination (see, e.g., refs^{1,2}), two, viz. the titrimetric^{3,4} and gravimetric⁵⁻⁸ methods, are least instrumentation-demanding. In both of them, a liquid is allowed to fill up the pores, and the amount of liquid so used up is directly determined. In the titrimetric procedure, the liquid is added dropwise; while this liquid penetrates into the pores, the powder remains loose; the first excess liquid forms a film between the particles, and agglomeration of the powder takes place. In the gravimetric method, the particles are brought in contact with the liquid in its vapour form, and the vapours are allowed to condense in the pores of the solid. After the equilibrium (filling-up of the pores) is reached, the sample weight remains constant, independent of the exposure time and also of the relative vapour pressure used. The titrimetric and, particularly, the gravimetric measurements are rather easy to perform; the titrimetric analysis is also rapid enough.

In ref.¹, the titrimetric method in a modification by Mottlau and Fisher⁴ has been recommended for the determination of the specific pore volume of silica gel packings for liquid chromatography; the reported reproducibility and accuracy, however, are an order of magnitude poorer than as given in ref.⁴ The agreement between the results obtained by this method and those derived from the amount of vapours of liquid adsorbed near the saturated pressure (Gurvitsch's method), reported in ref.¹, is also rather poor.

When comparing different methods for the determination of pore volume, the values obtained by low-temperature condensation of liquid nitrogen vapours are usually regarded as reference data. The pore filling by condensing vapours of a liquid is described by Kelvin's equation,

$$d = -4\gamma V \cos \Theta / [RT \ln (p/p_0)], \quad (1)$$

where d is the diameter of the meniscus of condensate in a capillary at a relative vapour pressure p/p_0 , V and γ are the molar volume and surface tension of the liquid, respectively, and Θ is its contact angle on the solid at a temperature T ; R is the gas constant. If the monomolecular layer thickness of the liquid is negligible with respect to the pore radius, d has the meaning of the diameter of the largest filled pore². For pores larger in size, where the difference in the pore filling caused by differences in the molecular size can be disregarded, the V_p value determined from the amount of nitrogen adsorbed at low temperatures should be as accurate as that determined from the condensation of vapours of any other liquid⁵⁻⁸.

During the titrimetric determination of V_p , the pores are filled with both a film of titrant and its condensing vapours. The equilibrium distribution of adsorbate in the pores of the solid then also must obey Kelvin's equation. Provided the liquid in the intergranular space and in the pores of the solid is in an equilibrium state at least in the titration end point, the pore volumes determined from the equilibrium gravimetric and titrimetric data should differ no more than the volume of liquid spent on the agglomeration of the adsorbent particles. According to Innes³, for the titration of silica-alumina based cracking catalysts 15–200 μm particle size this volume is negligibly low.

The aim of the present work was to seek whether the reproducibility reported⁴ for the titrimetric determination of the specific pore volume of alumina-based catalysts of larger particle size can be also attained for microparticulate silica gels. The accuracy of the titrimetric determination, a prerequisite of which is the establishment of the equilibrium in the titration end point, was assessed based on the agreement of the results with those of the gravimetric determination. The effect of the chemical modification of the silica gel on the reproducibility of measurement was also studied for both methods, and their applicability to the specific pore volume determination of chromatographic silica gels with values in excess of 1 ml g^{-1} was examined.

EXPERIMENTAL

The majority of experiments were performed with two commercial batches of irregular Silasorb silica gel (Lachema, Brno, Czechoslovakia), selected at random. According to manufacturer's data, the high surface area Silasorb 600 had a specific surface area of $S = 540 \text{ m}^2 \text{ g}^{-1}$, specific

pore volume $V_p = 0.70 \text{ ml g}^{-1}$ and mean pore diameter $D_p = 5.2 \text{ nm}$. It was separated on an Alpine A 100 MZR Multiplex zigzag separator into fractions with mean particle diameter ranging from 5.8 to 27.8 μm . The mean particle size of the fractionates was measured on a Sedigraph 5000 E instrument (Micromeritics, U.S.A.). Samples of chemically modified Silasorb (Silasorb C₂, C₈, C₁₈, Amin, Diol, and Nitril) were prepared from Silasorb 300 whose manufacturer's data were $S = 350 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.7 \text{ ml g}^{-1}$ and mean particle diameter $d_p = 10 \mu\text{m}$. Silasorb Amin was prepared so that the amine groups were protonated and their positive charge compensates with chloride anions. LiChrospher Si 100 (Merck, Darmstadt, F.R.G.), Separon SI VSK (Laboratorní přístroje, Prague, Czechoslovakia) and three samples of spherical silica gels with pore volumes larger than 1 ml g^{-1} (labelled A, B, and C) were also used.

Prior to the titrimetric as well as gravimetric measurements, the samples were dried for 2 h, the untreated silica gels at 150°C, the modified gels at 110°C. Distilled water, methanol of reagent grade purity (Lachema, Brno, Czechoslovakia) and n-octane of purity 95% or better (Jenapharm, G.D.R.) were employed for the pore volume measurements.

The closed titrating apparatus suggested by Mottlau and Fisher⁴ was modified as follows. The Erlenmeyer flask was replaced with a 100 ml cylindrical bottle with a flat bottom 40 mm in diameter, and a stirring bar 38 mm long was used. The orifice of the burette 2 ml in volume was connected flexibly with a syringe needle 0.4 mm o.d., which passed through a rubber stopper off the centre of the titrating vessel. The sample weight, 1–2 g in ref.⁴, was increased to 3–3.5 g. The titration dripping frequency was 15 drops per minute with water and 60 drops per minute with methanol. The stirring rate was 300 rpm.

During the gravimetric determination of the specific pore volume, the dry sample was equilibrated in a desiccator with vapours of a liquid placed on the bottom. The process was conducted at atmospheric pressure and room temperature ($22 \pm 2^\circ\text{C}$). One-gramme samples were accommodated in ground-in weighing bottles. Cetyltrimethylammonium bromide was added to methanol to reduce its saturated vapour pressure to $p/p_0 = 0.95$.

RESULTS

Titrimetric Determination of Specific Pore Volume

The titrimetric measurements were performed with water, n-octane, and methanol as titrants. Water has been recommended for this purpose in ref.¹. n-Octane was tested as a nonpolar low-volatile solvent with a considerably lower surface tension than water and with an appreciably bulkier molecule; its interactions with the carbonaceous modifying groups could be also expected to be free from nonidealities. Methanol was used with regard to the fact that in its size it approaches water more closely than other organic substances, and the chemically modified silica gels are wetted by it; its surface tension approaches that of n-octane but its vapour pressure at room temperature is about ten times higher than that of n-octane and five times higher than that of water.

When stirred, the microparticulate silica gels swirl and adhere to the walls of the vessel. This swirling was suppressed by adaptation of the stirring rate and increasing the amount of sample so that the stirring bar remained covered during its motion. Premature agglomeration, appreciable particularly during the titration with water,

was suppressed by an optimum combination of the stirring rate and the rate of addition of titrant, and by adding the titrant in small drops off the centre of the vessel. Before reaching the titration end point where irreversible sample agglomeration takes place, the rate of titrant addition had to be lowered considerably. Similarly as in ref.⁴, the determination of the end point was found to be affected significantly by the stirring rate. The silica gel aggregation in the titration end point also depended on the mean particle size and on the nature of the modifying groups. With titrants wetting the sample, neither the reproducibility nor the V_p value determined was affected by the course of the aggregation.

The reproducibility of the titrimetric determination was tested on six samples fractionated from a batch of the high surface area Silasorb 600, where the mean particle size varied from 5.8 to 27.8 μm . Water and methanol were used as titrants. One to three parallel portions were taken from each sample (Table I). After correction for the amounts of titrants present in the 100 ml titrimetric vessel in the vapour form, viz. 2.6 μl for water and 24 μl for methanol, the V_p value determined with methanol, viz. 0.65₂ ml g⁻¹, was 0.01 ml g⁻¹ higher than that determined with water.

During titrations of the chemically modified gels with water, the titration end point was only discernible for the silica gels carrying diol, cyano, and amine groups. The expected values were only obtained for silica gel modified with propylamine and propyldiol groups. The V_p value agreed with those measured with methanol and n-octane for Silasorb Amin. Silica gel modified with cyanopropyl groups accepted water well at the beginning of the titration and the end point was discernible similarly as with Silasorb Diol and Silasorb Amin; the pore volume, however, was considerably lower than as measured with the organic titrants. The expected pore

TABLE I

Reproducibility of the titrimetric determination of the specific pore volume of Silasorb 600

d_p μm	V_p^a , ml g ⁻¹		d_p μm	V_p^a , ml g ⁻¹	
	H ₂ O	CH ₃ OH		H ₂ O	CH ₃ OH
27.8	0.64 ₃	0.68 ₁	15.6	0.65 ₂	—
27.8	0.63 ₂	—	10.5	0.62 ₇	0.67 ₁
19.4	0.63 ₈	0.68 ₃	6.6	0.65 ₃	—
19.4	0.65 ₅	—	6.6	0.62 ₇	—
15.6	0.64 ₉	0.67 ₈	6.6	0.63 ₈	—
15.6	0.65 ₁	—	5.8	0.62 ₃	0.66 ₅

^a Uncorrected values; average for H₂O and CH₃OH: 0.64₁ and 0.67₆ ml g⁻¹, respectively, relative standard deviation: 1.56 and 1.26%, respectively.

volume of Silasorb 300 after its chemical treatment was assessed based on the results of elemental (C, N) analysis of the samples, taking into account the structures of the modifying groups given in ref.¹. During titrations with methanol and n-octane the titration end point was always sharp; the V_p data were mutually consistent for all the modified silica gels used (Table II).

Gravimetric Determination of Specific Pore Volume

The simplest possible arrangement was used for the gravimetric determination. For Silasorb 600, the adsorption equilibrium in methanol vapours (whose saturated pressure is $p_0 = 13.5$ kPa at 22°C) established in nearly two days, adsorption of water vapours ($p_0 = 2.63$ kPa) took seven days.

The reproducibility of the gravimetric measurement of V_p was tested with the unmodified Silasorb 600 at the saturated pressure of water and methanol vapours, and also at a relative pressure of methanol vapours 0.95. The reproducibility of the determination performed simultaneously in parallel was good (Table III). The capillary condensation⁷ of the saturated methanol vapours between the silica gel particles was insignificant with respect to the measured pore volume; the liquid was qualitatively detectable. Sample equilibrated with saturated methanol vapours to constant weight agglomerated in the same manner as in the end point of the titrations, whereas on the equilibration at a relative methanol pressure of 0.95, no agglomeration took place even after a 10 days' exposure. This difference at $p/p_0 = 1$ and 0.95 was observed for all silica gel samples.

TABLE II

Titrimetric and gravimetric determination of the specific pore volume of chemically modified silica gels prepared from Silasorb 300

Adsorbent	$(V_p)_{\text{titr}}, \text{ ml g}^{-1}$			$(V_p)_{\text{grav}}, \text{ ml g}^{-1}$		
	CH_3OH	C_8H_{18}	H_2O	H_2O^a	CH_3OH^a	CH_3OH^b
Silasorb 300	0.78 ₀	0.82 ₂	0.77 ₈	0.76 ₀	0.79 ₉	—
Silasorb C ₂	0.65 ₅	0.66 ₅	0.6—0.8	0.02 ₉	0.66 ₅	0.65 ₅
Silasorb C ₈	0.47 ₃	0.48 ₅	—	0.02 ₉	0.47 ₂	0.44 ₅
Silasorb C ₁₈	0.29 ₅	0.31 ₈	—	0.02 ₇	0.30 ₇	0.28 ₇
Silasorb Amin	0.69 ₁	0.68 ₉	0.68 ₆	0.66 ₂	0.69 ₅	0.67 ₀
Silasorb Diol	0.47 ₈	0.48 ₀	0.45 ₆	0.49 ₂	0.49 ₃	0.48 ₀
Silasorb Nitril	0.57 ₇	0.56 ₄	0.16 ₁	0.05 ₂	0.58 ₄	0.57 ₀

^a $p/p_0 = 1$; ^b $p/p_0 = 0.95$.

Chemical modification of the silica gel surface affected appreciably the condensation of water in the pores. Only the gels with amine and diol groups exhibited hydrophilic behaviour, whereas the remaining gels behaved as hydrophobic materials. A difference in the ability to accept water vapours and water liquid was observed for silica gel modified by reaction with trimethylchlorosilane. Silasorb C₂ exhibited hydrophilic behaviour with respect to liquid water, whereas with respect to water vapours its behaviour was virtually equally hydrophobic as that of silica gel carrying octyl or octadecyl groups. Silica gel with cyanopropyl groups was also hydrophobic to condensing water vapours, although to a lesser extent than Silasorb C₂.

Methanol condensed well in the pores of all the chemically modified silica gels, and the pore volumes measured agreed well with those found by titration (Table II).

Pore Volume Determination for Wide-Porous Silica Gels

Samples with specific pore volumes in excess of 1 ml g⁻¹ exhibited a marked tendency to premature agglomeration during their titration with water. The V_p values determined with water and with n-octane were mutually consistent for all samples (Table IV) whereas those determined with methanol were systematically higher, this difference increasing with increasing mean pore diameter.

After two weeks' equilibration in methanol vapours at $p/p_0 = 0.95$, the pores were completely filled for those gels only whose mean pore diameter was at least 50% lower than the meniscus diameter calculated according to Eq. (1); the rate of pore filling decreased with increasing mean pore diameter (Table V). All samples equilibrated in saturated methanol vapours agglomerated on their agitation. The pore volumes after agglomeration agreed well with those obtained by titration with methanol.

TABLE III

Reproducibility of replicate gravimetric determination of specific pore volume V_p (ml g⁻¹) of Silasorb 600, screened fraction $d_p = 10.5 \mu\text{m}$

	CH ₃ OH ^a	CH ₃ OH ^b	H ₂ O ^b
	0.66 ₄	0.67 ₀	0.66 ₂
	0.66 ₁	0.67 ₁	0.65 ₆
	0.66 ₉	0.67 ₁	0.65 ₆
	0.66 ₀	0.67 ₂	—
	0.66 ₀	0.67 ₀	—

^a $p/p_0 = 0.95$; ^b $p/p_0 = 1.0$.

DISCUSSION

The titrimetric apparatus and procedure described in ref.⁴ can be adapted to conform to the properties and behaviour of microparticulate silica gels. If a titrant wetting the sample well is used, premature sample agglomeration does not take place and a sharp titration end point is observed; the relative standard deviation of such measurements is lower than 2%. This reproducibility is comparable to that reported in ref.⁴ for coarser alumina-based catalysts. In the gravimetric method the difficulties brought about by the very low grain size of the samples are circumvented and the error due to the subjective determination of the end point is eliminated. The reproducibility of the gravimetric determination of V_p is thus still better, particularly if the replicate determinations are carried out simultaneously (Tables I and III).

The accuracy of the titrimetric determination is the higher the more closely the volume of the added titrant approaches the sample pore volume. Evaporation of titrant and overtitration causing sample agglomeration in the titration end point lead to apparently higher pore volumes; apparently lower values, on the other hand, are obtained if the very narrow pores are filled incompletely by the too bulky molecules of titrant² or if the largest pores across the whole sample bulk remain incompletely filled after the sample agglomeration, if the equilibrium of the vapour tension in the intergranular space and in the pores has not established.

Numerical corrections for the evaporated titrant can be made if a closed titrimetric apparatus is used. The experimental results confirm the observation by Innes³ that the volume of liquid taken up for the sample agglomeration is very low. Gravimetric measurements with Silasorb 600 in methanol vapours revealed that for this silica gel, this volume is not larger than 8 μl of liquid per gramme of sample.

TABLE IV

Titrimetric and gravimetric determination of the specific pore volume for silica gels with specific pore volumes higher than 1 ml g^{-1}

Sample	S^a m^2 g^{-1}	V_p^a ml g^{-1}	d_p^a μm	$(V_p)_{\text{titr}}$, ml g^{-1}			$(V_p)_{\text{grav}}$, ml g^{-1}	
				CH_3OH	H_2O	C_8H_{18}	CH_3OH^b	CH_3OH^c
LiChrospher SI 100	536	1.20	10	1.18	1.13	1.15	1.15	1.15
Separon SI VSK	500	1.75	14	1.57	1.48	1.48	1.51	1.56
A	322	1.40	17.3	1.40	1.33	1.32	0.99	1.38
B	326	1.66	20.4	1.80	1.62	1.59	0.74	1.78
C	300	1.70	22.6	1.98	1.84	1.86	0.58	2.01

^a Manufacturer's data; ^b $p/p_0 = 0.95$; ^c $p/p_0 = 1$.

Tables I, II, and IV demonstrate that the differences in the molecular size of the titrant do not play any significant role in the pore filling, because if the reverse were true, the V_p value found with the use of water would have to be higher than that found with the use of methanol, at least for Silasorb 600 with $D_p = 5.2$ nm. Actually, the value measured with methanol was higher, even after correction for the amount of the methanol and water vapours present in the titrimetric vessel. This can be so explained that in the end point of titration with water, the pores were not completely filled over the whole sample bulk. The more perfect pore filling with methanol can be ascribed to the higher vapour tension of this titrant, making for the establishment of the equilibrium state. This is consistent with the results of determination of V_p summarized in Table IV as well as with the rate of the pore filling for pores of different diameter in dependence on the liquid vapour tension (Table V).

Innes' assumption that liquids with a higher surface tension would give a sharper titration end point³ was not confirmed. For the titration of Silasorb 600 and Silasorb 300 with methanol or n-octane the end point was as sharp as for the titration with water, and for the titration of silica gels whose pore volumes were in excess of 1 ml g^{-1} , even sharper. This is probably due to the easier film formation of the organic solvent on the gel particles as compared to water.

The gravimetric method requires a sufficiently high vapour pressure of the liquid employed. Completeness of the pore filling can be only evidenced by a comparison with the results obtained at a higher relative vapour pressure (Table V). For equilibration at the saturated vapour pressure the equilibrium is indicated by sample agglomeration on its agitation. If the sample is constantly in a temperature equilibrium

TABLE V

Volume of methanol (ml) condensed in 1 g of sample, in dependence on the mean pore volume and relative pressure of methanol vapours

Sample	D_p^a nm	Exposure (days) at $p/p_0 = 0.95$				Exposure (days) at $p/p_0 = 1$		
		2	7	10	14	6	7	17
		LiChrospher SI 100	8.8	0.82	0.97	1.06	1.15	1.15
Separon SI VSK	12.6	1.03	1.30	1.43	1.51	1.54	1.54	1.56
A	17.4	0.51	0.60	0.73	0.99	1.28	1.34	1.38
B	22.1	0.41	0.48	0.58	0.74	0.96	1.04	1.78
C	26.4	0.35	0.42	0.48	0.58	0.93	1.00	2.01

^a Calculated as $D_p = 4V_p/S$ employing the specific surface area values and specific pore volumes determined with the use of methanol, given in Table IV.

with the evaporated liquid during the equilibration, the intergranular condensation does not increase so as to spoil the measurement even if the equilibration in saturated vapours has been conducted for a very long period of time and the temperature of the whole system has changed by several degrees Centigrade (Tables IV and V).

From the reproducibility and accuracy points of view, the titrimetric and gravimetric methods of determination of the specific pore volume are comparable. The former is suitable for routine measurements of large sample series, particularly if it is desired that the results be available as soon as possible. When working with a closed apparatus, it is advised to choose a volatile titrant with a not very high surface tension, wetting the sample well; methanol suits well to this purpose for both untreated and modified silica gels. The gravimetric method is suitable where the titrimetric approach meets with difficulties, for occasional measurements of few samples and in cases where the results need not be available very soon.

REFERENCES

1. Unger K. K.: *Porous Silica*. Elsevier, Amsterdam 1979.
2. Gregg S. J., Sing K. S. W.: *Adsorption, Surface Area and Porosity*, 2nd ed. Academic Press, London 1982.
3. Innes B. W.: *Anal. Chem.* 28, 332 (1956).
4. Mottlau A. Y., Fisher N. E.: *Anal. Chem.* 34, 714 (1962).
5. Bachman W.: *Z. Anorg. Chem.* 79, 202 (1913).
6. Rossini F. D., Mair B. J., Streif A. J.: *Hydrocarbons from Petroleum*, p. 135, 142. Reinhold, New York 1953.
7. Benesi H. A., Bonnar R. U., Lee C. F.: *Anal. Chem.* 27, 1963 (1955).
8. Bikerman J. J.: *Surface Chemistry*, 2nd. ed., p. 204. Academic Press, New York 1958.

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